

**Study on the Effectiveness of Ionic Liquid as
Low Dosage Hydrate Inhibitor (LDHI) for
Flow Assurance in Pipeline.**

by

LEE KUO CHUN
(Student ID: 10697)

Mechanical Engineering Department

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Study on the Effectiveness of Ionic Liquid as Low Dosage Hydrate Inhibitor (LDHI) for Flow Assurance in Pipeline.

by

Lee Kuo Chun

A project dissertation submitted to the
Mechanical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(MECHANICAL ENGINEERING)

Approved by supervisors:

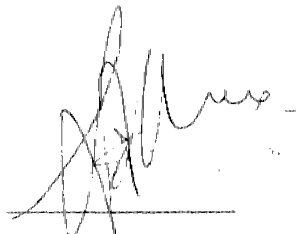

(**Dr. Azuraïen Jaafar**)
AZURAIEN JAPPER @ JAAPAK
Lecturer
Mechanical Engineering Programme
UNIVERSITI TEKNOLOGI PETRONAS
Bandar Seri Iskandar, 31750 Tronoh
Perak Darul Ridzuan, Malaysia

**UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK**

December 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

A handwritten signature in black ink, appearing to read 'LEE Kuo Chun', written over a horizontal line.

LEE KUO CHUN

22/1/2020

ABSTRACT

This research project is an experimental approach to study the effectiveness of ionic liquids as low dosage hydrate inhibitors (LDHI) for flow assurance in pipelines. In addition, this project is also aimed to gain a better understanding about gas hydrates and choosing new potential ionic liquids as LDHI. Gas hydrates are solid crystalline compounds formed by water and molecules like natural components at low temperature and high pressure conditions. Hydrates formation often occur and block gas pipelines which causes production failure and safety hazards.

The conventional method to prevent the formation of gas hydrates is by using large quantities of thermodynamics inhibitors, which is expensive and dangerous to the environment. Thus, suitable new class of ionic liquids such as low dosage hydrate inhibitor (LDHI) that are strong and effective needs to be discovered to replace the conventional method. The criteria of ionic liquids were studied – stabilities, hydrophilic, tuneable organic cations and anions and extremely low vapour pressures.

In this study, parameters such as kinetic rate and induction time need to be experimentally considered and investigated by using High Pressure Kinetics Measurement (HPKM) for bulk volume. Currently for HPKM, the temperature at 273.65 K and pressure at 35bar is selected to be operating condition for the experiment of hydrate formation as data were recorded every second by data acquisition system. This experiment was continued by adding LDHI (0.1wt%, 0.5wt%, 1.0wt %) and using different pressures (25bar, 30bar and 35bar) to test the effects. However, 10.0 wt% high concentration of EMIM BF₄ is used for the study of ionic liquid effectiveness as thermodynamic inhibitors.

The findings of this work will contribute to a more environment friendly and economical hydrate inhibitors for usage in the oil and gas industrials.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my greatest gratitude towards God for His blessing to this FYP project. I also would like to thank both my supervisors, Dr Azuraïen Jaafar and Dr Khalik, for their continuous support, advice and guidance in completing this project.

I would like to take this opportunity to thank UTP technicians and Security Department for their approval to enter the laboratory. Besides, I would like to thank PETRONAS Ionic Liquid Center for contributing the ionic liquid for this project. Last but not least, thanks to my family and colleagues for their precious help, comments, suggestions and support to do my best.

Thank you.

Chapter 3.0 METHODOLOGY

3.1 Chemical Identification	12
3.2 Tools and Software Identification	13
3.3 Experiment Procedure for High Pressure Kinetics Measurement	14
3.4 Research and Experiment Methodology	16
3.5 Project Activities	17
3.6 Example calculation for 1-Ethyl-3-methylimidazolium tetrafluoroborate, EMIM BF ₄ at 0.1wt%	18
3.6 Gantt Chart for FYP 2	19
3.7 Key Milestones and Dates	19

Chapter 4.0 RESULTS AND DISCUSSION

4.1 Experiments status and example of CO ₂ hydrates	20
4.2 Results	20
4.2.1 Data Analysis for experiments at pressure, <u>25bar</u> and temperature, 2 °C	21
4.2.2 Data Analysis for experiments at pressure, <u>30bar</u> and temperature, 2 °C	24
4.2.3 Data Analysis for experiments at pressure, <u>35bar</u> and temperature, 2 °C	27
4.3 Discussion	30
4.4 Results on the induction time for all pressure and concentrations	31
4.5 Data Analysis for <u>additional experiment</u> (10.0 wt% concentration) at pressure, <u>30bar</u> and temperature, 2 °C	32

Chapter 5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion	36
5.2 Recommendation for Future Works Expansion and Continuation	37

REFERENCES	38
-------------------	-----------

APPENDICES	40
-------------------	-----------

LIST OF FIGURES

Figure 1.1:	Hydrate plug formation via aggregation in an Oil-dominated system	1
Figure 1.2:	Example of hydrate blockage in pipelines	2
Figure 2.1:	Schematic Diagram of Pressure Changes with Time during Hydrate Formation	4
Figure 2.2:	Hydrate structure and hydrates solid examples	5
Figure 2.3:	Cages and Coordination Number in Structure I, II and H.	6
Figure 2.4:	Effect of additional methanol on hydrates formation	8
Figure 2.5:	Three Phase Equilibrium Data for Carbon Dioxide and Water Hydrate System	11
Figure 2.6:	Three Phase Equilibrium Data for Carbon Dioxide Hydrate Formation	11
Figure 3.1:	Schematic Illustration of the Apparatus for the High Pressure Kinetics Measurement (HPKM)	13
Figure 3.2:	Micropipette used to acquire precise amount of liquid from Block 4 level 1	13
Figure 3.3:	HPKM system with magnetic stirrer.	15
Figure 3.4:	Computer + Data Acquisition System	15
Figure 3.5:	Cryostat (cooling device)	15
Figure 3.6:	CO ₂ gas tank	15
Figure 3.7:	Reactor Submerged in Thermostatic Bath	15
Figure 3.8:	Experiments station at Block 5. 00. 01 Laboratory	15
Figure 3.9:	Flowchart of Research Methodology	16
Figure 3.10:	Flowchart of Experimental works	16
Figure 4.1:	Example of CO ₂ hydrate formation in reactor @ 30bar	20
Figure 4.2:	CO ₂ hydrate formation outside of reactor @ 30bar	20
Figure 4.3:	CO ₂ hydrate formation outside of reactor @ 30bar	20
Figure 4.4:	Without Ionic Liquid @ 25bar	21
Figure 4.5:	With 0.1wt% EMIM BF ₄ @ 25bar	21

Figure 4.6:	With 0.5wt% EMIM BF ₄ @ 25bar	21
Figure 4.7:	With 1.0wt% EMIM BF ₄ @ 25bar	21
Figure 4.8:	CO ₂ Hydrate Temperature VS Time @ 25bar	22
Figure 4.9:	CO ₂ Hydrate Pressure VS Time @ 25bar	23
Figure 4.10:	Without Ionic Liquid @ 30bar	24
Figure 4.11:	With 0.1wt% EMIM BF ₄ @ 30bar	24
Figure 4.12:	With 0.5wt% EMIM BF ₄ @ 30bar	24
Figure 4.13:	With 1.0wt% EMIM BF ₄ @ 30bar	24
Figure 4.14:	CO ₂ Hydrate Temperature VS Time @ 30bar	25
Figure 4.15:	CO ₂ Hydrate Pressure VS Time @ 30bar	26
Figure 4.16:	Without Ionic Liquid @ 35bar	27
Figure 4.17:	With 0.1wt% EMIM BF ₄ @ 35bar	27
Figure 4.18:	With 0.5wt% EMIM BF ₄ @ 35bar	27
Figure 4.19:	With 1.0wt% EMIM BF ₄ @ 35bar	27
Figure 4.20:	CO ₂ Hydrate Temperature VS Time @ 35bar	28
Figure 4.21:	CO ₂ Hydrate Pressure VS Time @ 35bar	29
Figure 4.22:	Induction VS Pressure for CO ₂ Hydrate Formation	31
Figure 4.23:	Concentration VS Induction time for CO ₂ Hydrate Formation	28
Figure 4.24:	With 10.0 wt% EMIM BF ₄	32
Figure 4.25:	CO ₂ Hydrate Pressure VS Time (including 10 wt%)	33
Figure 4.26:	CO ₂ Hydrate Temperature VS Time (including 10 wt%)	33
Figure 4.27:	Induction time of CO ₂ Hydrate Formation (including 10 wt%)	34
Figure 4.28:	Concentration VS Induction time for CO ₂ Hydrate Formation (including 10 wt%)	35
Figure 5.1:	2 different sizes of magnetic stirrers.	37
Figure 5.2:	Difficulties to place both thermostatic bath and magnetic stirrer plate below the reactor	37

LIST OF TABLES

Table 2.1:	Analysis and ionic liquids that have been studied in journals	10
Table 3.1:	Ionic liquid studied in this work	12
Table 3.2:	Materials involved with their suppliers and phases.	12
Table 3.3:	Gantt chart for the Second Semester Project Implementation	19
Table 4.1:	Experiments start date.	20
Table 4.2:	Induction time of Carbon Dioxide hydrate Formation at various pressures	31
Table 4.3:	Induction time of Carbon Dioxide hydrate Formation at various pressure	34

Nomenclature

The following abbreviations and acronyms are used throughout the text:

AA	Anti-Agglomerant hydrate inhibitor
bbl	barrel (42 US gallons = 0.159 m ³)
bcpd	barrels of condensate per day
bopd	barrels of oil per day
bpd	barrels per day
bwpd	barrels of water per day
CAPEX	capital expenditure
CI	corrosion inhibitor
CO ₂	carbon dioxide
FPSO	Floating Production Storage and Offloading vessel
GOR	Gas to Oil Ratio
H ₂ S	hydrogen sulfide
in	inch = 2.54 cm
KHI	Kinetic Hydrate Inhibitor
Km	Kilometer (1 KM = 0.621 mile)
L	Liter (1 Liter = 0.264 Gallons)
LDHI	Low Dosage Hydrate Inhibitor
m	Meter (1 meter = 3.28 ft)
MEG	ethylene glycol
MeOH	methanol
MM	million
MMscfd	million standard cubic feet per day
mpy	mils per year (corrosion rate)
OPEX	operational expenditure
PI	paraffin inhibitor
ppm	parts per million
psig	pounds per square inch (gauge)
scf	standard cubic feet
stb	standard barrel (1 barrel = 0.159 m ³)
THI	Thermodynamic Hydrate Inhibitor

CHAPTER 1.0

INTRODUCTION

1.1 Background of Study

In the production of natural gas fields and oil fields, flow assurance is most critical task during deep water energy production because of the high pressure and low temperature ($\sim 4^{\circ}\text{C}$) involved. This can cause scale deposition such as the formation of gas hydrates that causes catastrophic blockages and restrictions which can lead to the impairment of flow.

In a survey of 110 energy companies, flow assurance was listed as the major technical problem in offshore energy development.^[6] Every few years, somewhere in the world a major injury occurs, a major equipment or asset damage is done (financial loss), due to hydrates.

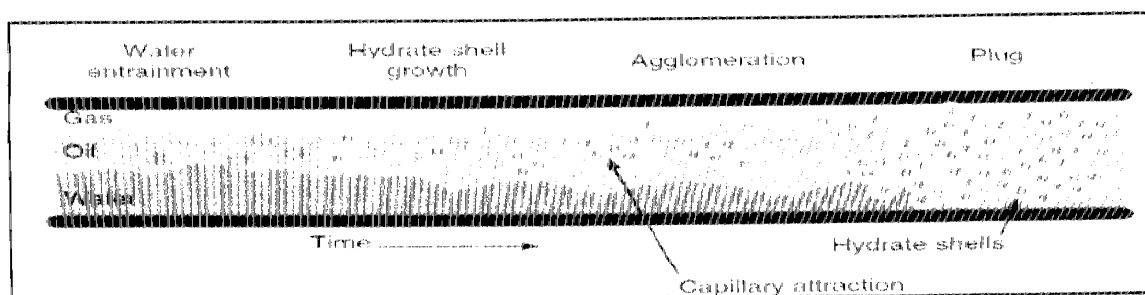


Figure 1.1: Hydrate plug formation via aggregation in an oil-dominated system

Gas hydrates are crystalline solid compounds formed by water and natural gas (e.g., methane) or volatile liquids under suitable temperature and pressure conditions (2000 psig). The gas molecules (guests) are trapped in water cavities (host) that are composed of hydrogen-bonded water molecules.^[6] Gas hydrates are known to occur in vast amounts in nature, mainly methane-hydrate in the sea bed and below permafrost.

Several techniques to remove hydrates formation are available, such as thermal stimulation, depressurization and chemical inhibitor injection. However, chemical inhibitor has been quoted as the most economically viable option. Two types of inhibitors that are used nowadays: thermodynamics and kinetic inhibitors. Thermodynamic inhibitors are expensive and hazardous. Thus, new low dosage hydrate inhibitors (LDHI), “green technologies” ionic liquids (ILs) are studied due to their properties such as tuneable organic behaviour, stabilities, hyper low vapour pressures and environmental friendliness.

1.2 Problem Statements

In general, gas hydrate can cause blockage in pipelines and processing facilities while to remove hydrate plugs is difficult to achieve. The oil and gas industry spends about 500 millions of dollars annually on inhibitors (e.g., methanol or glycol) or as much as \$48 MM to insulate a single subsea pipeline. ^[3]



Figure 1.2: Example of hydrate blockage in pipelines

For this FYP 1, it is crucial to study ionic liquids and its properties as low dosage hydrate inhibitors (LDHI). This is followed by selecting the most suitable ILs based on their criterion. The understanding of the selected ILs as LDHI through investigating the effectiveness by measuring the suitability on properties such as kinetic rate and induction time is vital for this project. Some of the criteria for a good LDHI are the safety, effect to environment, hydrophilic behaviour, low cost, operation complexity and etc.

1.3 Objective

This report studies the different aspects of gas hydrate and the functions of Ionic Liquids as inhibitors to achieve the following objectives:

- To study the formation of gas hydrates within the hydrate formation region at low temperature and high pressure condition.
- To study the behaviour and properties of ionic liquids as LDHI.
- To run experiments with selected ionic liquids as LDHI to show the effect on hydrate formation.

1.4 Scope of Study

The scope of the research is summarized as follows in order to achieve the objectives within the time frame and funds allocated:

1. Conducting research on the theory and terms related to hydrate formation and inhibitors.
2. Identification of appropriate ionic liquids as LDHI.
3. High Pressure Kinetics Measurement (HPKM) system is used to measure the induction time of CO₂ hydrate formation while LabVIEW 8.5 software is used to record data such as the pressure and temperature of the experiment. Thus, thermodynamics knowledge on phase behaviour of carbon dioxide hydrate formation is greatly useful for this project. Besides, calculations involving concentration of CO₂ and Ionic Liquids (0.1wt%, 0.5wt%, 1.0wt %), rate constant and etc.

1.5 The Relevancy of the Project

- Thermodynamics 1
- Thermodynamics 2
- Fluid Mechanics
- Reservoir Engineering

1.6 Feasibility of the Project within the scope and time frame

- Related topics (articles, books, journals, research papers and websites)
- Ionic Liquids available at Chemical Department Blocks and PETRONAS Ionic Liquid Center at Block 4.
- High Pressure Kinetic Measurement equipment available at Block 5 (provided HSE briefing).

Since the necessary materials and equipment are available for use, the project can be done within the scope and time frame.

CHAPTER 2.0

LITERATURE REVIEW

2.1 Hydrate Mechanism

The hydrate formation can be divided into 2 processes - nucleation process and stable growth process.^[11] Hydrate nucleation process is a process of formation and growth of hydrate nuclei to a critical size. The simultaneous growths of water and gas molecule act as precursors to hydrate nuclei formation. The gas hydrate formation is a phase transition process which requires a supersaturated environment for hydrate to form. The guest molecules gas will dissolve in liquid water to build supersaturated condition through the liquid phase or locally near the interface between guest molecule gas and liquid water. At some point during dissolution, the precursors of hydrate phase (nuclei) appear. The nuclei will tend to grow if sufficient gas is present in the system. This nucleation process will continue to grow until the nuclei achieve a critical size. Induction time is one of parameter that is usually used to characterize the hydrate nucleation process.^[11] It is the time elapsed during the nucleation process which includes the formation of gas water cluster and their growth to stable nuclei with a critical size. The induction time can be obtained by observing the **pressure-time** relationship during hydrate formation.

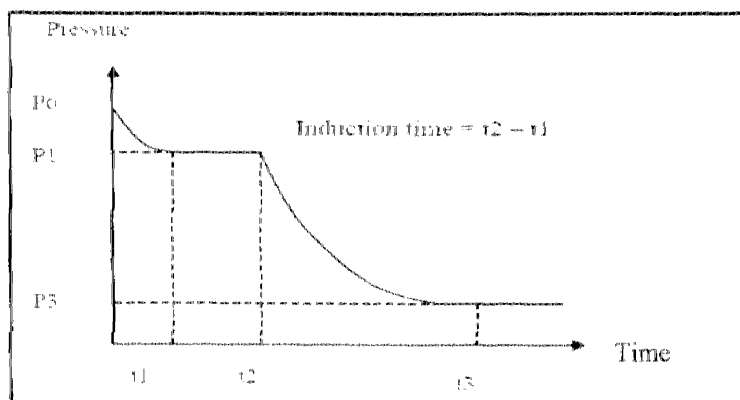


Figure 2.1: Schematic Diagram of Pressure Changes with Time during Hydrate Formation^[11]

Hydrate growth is a process that refers to the growth of stable hydrate nuclei as solid hydrates. Mass and heat transfers play important roles in hydrate growth process. The sudden pressure drop that occurs during the formation of hydrate indicates the hydrate growth (Figure 2.1) due to consumption of guest molecule to form hydrate structure. When the pressure of the system remains unchanged for couple of hours, this indicates that the hydrate formation is already complete.

2.2 Gas Hydrate

Gas hydrate is a crystalline solid compound formed in the mixture of **water** and non- or slightly polar low molecular weight **natural gases** or volatile liquids under suitable **temperature** (5–25°C) and **pressure** conditions (2000 psig). There is no chemical reaction during this hydrate formation, but the hydrogen bonded network creates cavities that are filled with guest molecules. Low molecular weight gases such as nitrogen, carbon dioxide, methane, ethane, propane, hydrogen sulfide are suitable guest molecules for hydrate formation as they are generally stable at low temperature and high pressures and are present in natural gas.

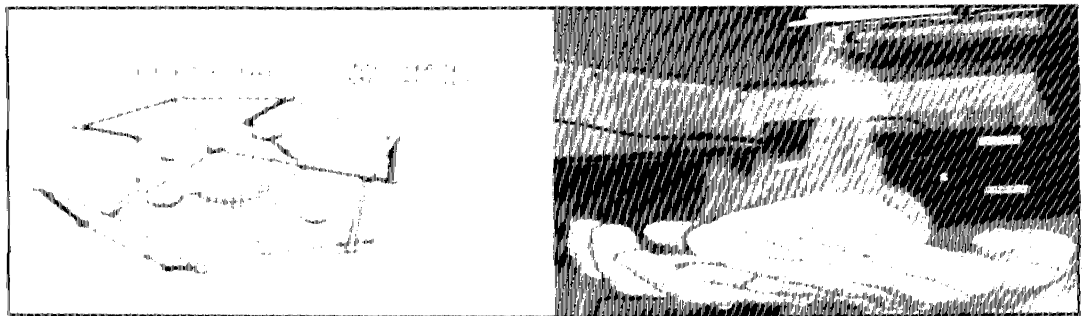


Figure 2.2: Hydrate structure and hydrates solid examples

Difference between gas hydrate and ice:

(Please refer to Appendix 2 – Comparison of Properties of Ice, sI and sII hydrate)

1. Gas hydrate can be formed at temperatures above 0°C while ice cannot.
2. Water molecules diffuse two orders of magnitude slower in hydrates than in ice.
3. **Mechanical Strength** - Hydrate is more than 20 times stronger (creep resistant) than ice.
4. **Elastic Properties** - Methane hydrate is significantly more compressible than ice.
5. **Thermal Properties** - Large thermal expansivity of hydrate is caused by the guest molecule, with the different arrangements of oxygen atoms in the hydrate and ice playing only a minor role.

- There are three common crystallographic structures for gas hydrates (differ in type and size of cavities and shape):
 - Structure I (sI) - simplest**
 - Structure II (sII) - complicated**
 - Structure H (sH) - less common**
- SI is a centered face cubic system which appear with light components such as methane, CH₄ or carbon dioxide CO₂
- SII is diamond type with 24 cavities per mash
- SH is hexagonal type constituted of 6 cavities.

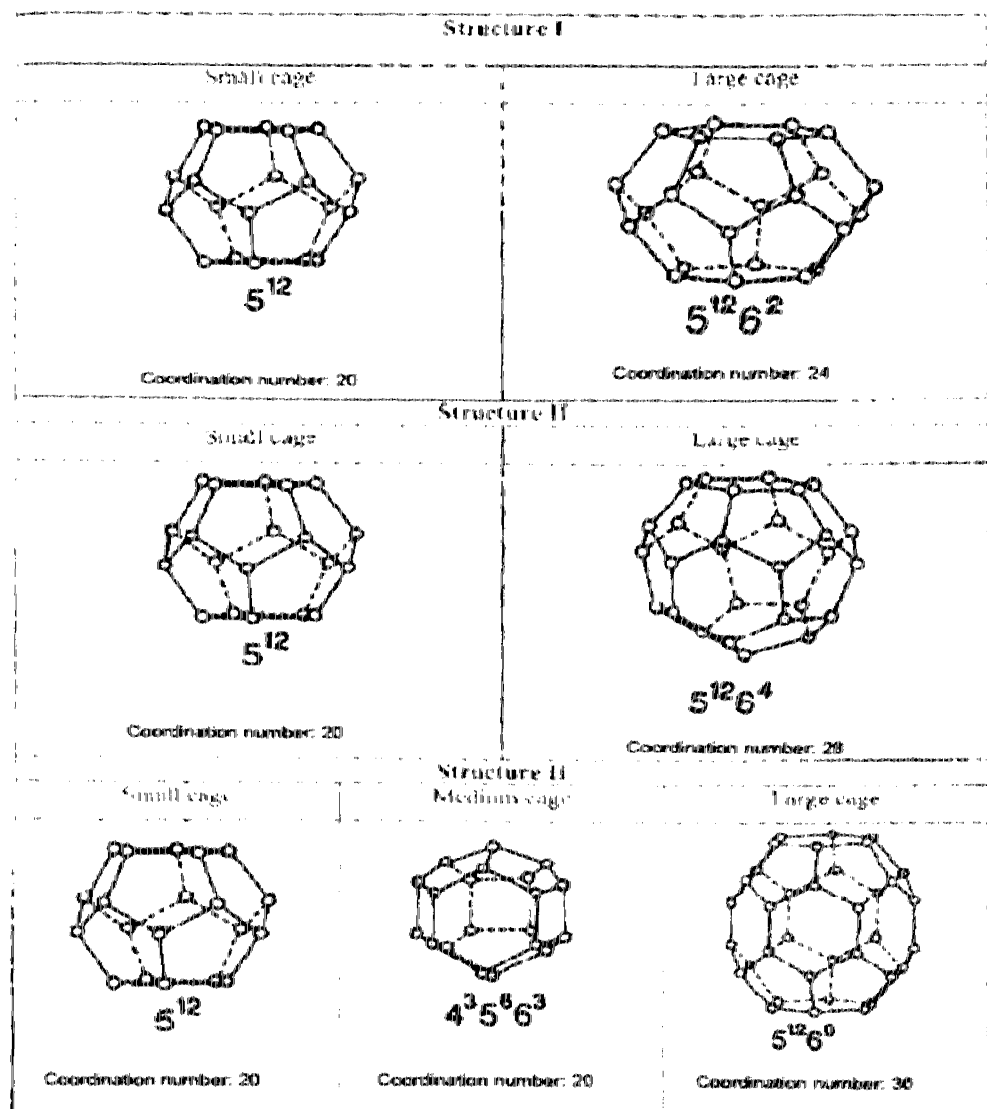


Figure 2.3: Cages and Coordination Number in Structure I, II and H. [8]

2.3 Current methods to mitigate the hydrate formation (plugs) in pipeline:

1. Hydraulic methods- Depressurization

- system pressure may be decreased below the hydrate-formation pressure with system-pressure drops at high temperature points (bottomhole chokes). Resulting in lower density but decreases the transportation efficiency.

2. Thermal methods

- Maintaining high temperatures keeps the system in the hydrate-free region. High reservoir fluid temperature may be retained through insulation and pipe bundling or heat may be added through hot fluids or electrical heating.

3. Removal of water or natural gas

- Separation removes free water. Water condensation from the gas phase is prevented by drying the gas. But it is not feasible as we definitely won't remove the natural gas (methane, propane, etc.) as those are the natural gases that we want.

4. Mechanical methods

- Physical and mechanical equipments are used such as coiled tubing, drilling through the plugs and etc.

5. Chemical methods

- Injection of Thermodynamic Inhibitors and Kinetic Inhibitors are used or reactive chemicals that generate heat that will be used to heat up the pipelines.

2.4 Chemical Inhibitors

Inhibitors are used to prevent and eliminate the formation of gas hydrate. Different types of inhibitors show different characteristics, effect on hydrate formations and the effectiveness. There are two types of inhibitors that are used nowadays: thermodynamics and kinetic inhibitors.

• Thermodynamic inhibitors

The most extensively used thermodynamic inhibitors (THI) are methanol, mono-ethylene glycol, diethylene glycol, and some other electrolytes. Inhibitor molecule or ion will compete with the water molecule, changing the thermodynamic equilibrium of water and hydrocarbon molecule (changing the chemical potential of hydration),

and prevent the formation of hydrate by moving the phase equilibrium curves to lower temperature and higher pressure. E.g., the hydrate-aqueous liquid-vapor equilibrium (HLVE) curve. Thus, the hydrate will become instable, decomposed and can be separated easily. Thermodynamic methods using methanol and glycol are costly in offshore developments and onshore processing facilities because of the high treatment amounts required (10–50% of the water phase) and this method has created many environmental and logistical issues.

Below is an example on the effect of methanol (THI):

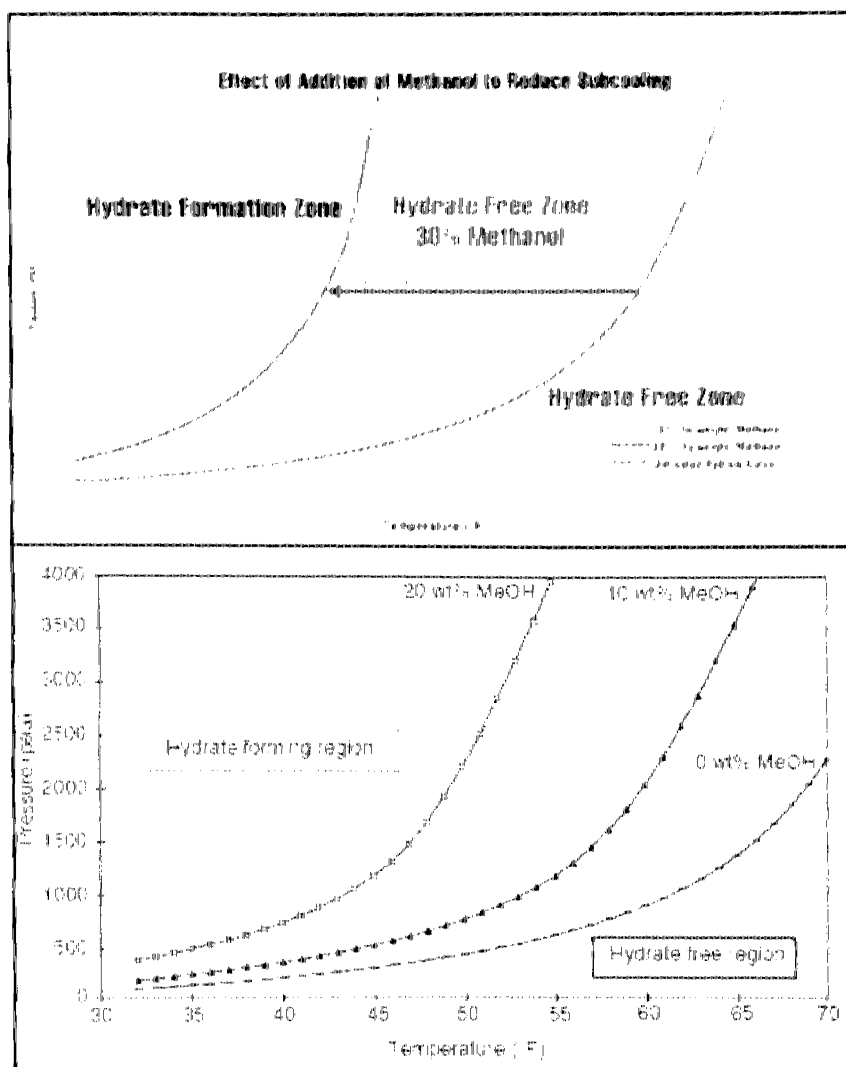


Figure 2.4: Example on effect of additional methanol on hydrates formation

- **Kinetic inhibitors**

It is also known as LDHI, example, Kinetic inhibitors (KHIs) and Anti-agglomerants (AAs). KHIs prevent and delay the hydrate nucleation and crystal growth so that there is enough time to transfer the fluid to the process facilities before the hydrate formation occurs. Some the commercial KHIs are based on water-soluble polymer. Meanwhile, AAs do not prevent hydrate formation process but they prevent the agglomeration and deposition of hydrate crystals such as transportable hydrate slurry that is formed in a liquid hydrocarbon phase.^[12]

Emulsification between the water phase and the oil phase will occur to prevent the agglomeration of the hydrate crystal before the formation of the hydrate. Among the advantages of kinetic inhibitors are: only small quantity of inhibitor is required, high efficiency, is not influenced by temperature.^[2] Kinetic inhibition methods are based on the injection of polymer-based chemicals at low dosages in the water phase.^[2]

Xiao et al.^[2] have reported preliminary results for five imidazolium-based ionic liquids as dual function thermokinetic inhibitors. They found that ionic liquid can function as LHDH at 0.1–1.0 wt.% of the overall concentration. This is a significant reduction when compared to the 10–50 wt% needed for thermodynamic inhibitors or “anti-freezes” such as methanol, glycols or salts.^[12]

2.5 Ionic liquid (molten salts)

Ionic liquids (ILs) are organic salts with low melting point that are being considered as green replacements for industrial volatile organic compounds. The reputation of these solvents as ‘environmental friendly’ chemicals is based primarily on their negligible vapor pressure.^[7] Ionic liquids are attracting interest as a greener alternative to conventional hydrate inhibitors due to properties such as their stabilities, tuneable organic cations and anions, extremely low vapor pressures and ease of preparations from relatively inexpensive materials.

The uniqueness of the structural tenability of the cations and anions in the ionic liquids suggests that there is a great possibility for the potential application of the ionic liquids. Since the cations and anions of the ionic liquids can be chosen or tailored to **form hydrogen bonds with water**, it can interfere with the hydrate formation condition.

Table 2.1 -Analysis and ionic liquids that have been studied in journals

Journal	Symbol	Chemical Name
1. Chongwei Xiao, Hertanto Adidharma.: Dual function inhibitors for methane hydrate, Journal of University of Wyoming, Laramie, USA (2008). Analysis: <ul style="list-style-type: none"> This dual function is expected to make this type of inhibitors perform more effectively than existing inhibitors. Tetrafluoroborate ionic liquids are found to perform better than other ionic liquids and much better than PVP. The performance of EMIM-BF₄ is also found to be much better than those of Luvicap and purified PVCap. 	EMIM-BF ₄	1-ethyl-3-methylimidazolium tetrafluoroborate
	BMIM-BF ₄	1-butyl-3-methylimidazolium tetrafluoroborate
	EMIM-N(CN) ₂	1-ethyl-3-methylimidazolium dicyanamide
	EMIM-CF ₃ SO ₃	1-ethyl-3-methylimidazolium tetrafluoromethanesulfonate
	EMIM-EtSO ₄	1-ethyl-3-methylimidazolium ethylsulfate
2. Chongwei Xiao, NicoWibisono, Hertanto Adidharma.: Dialkylimidazolium halide ionic liquids as dual function inhibitors for methane hydrate, Journal of University of Wyoming, Laramie, USA (2010). Analysis: <ul style="list-style-type: none"> EMIM -Cl is the most effective thermodynamic inhibitor. Effectiveness of these ionic liquids is in the following order: EMIM-Cl > EMIM-Br > PMIM-I > BMIM-Cl > BMIM-Br > BMIM-I. For ionic liquids with same cations (BMIM or EMIM), the effectiveness is decreasing along the sequence: Cl > Br > I > BF₄ Inhibition effectiveness of ionic liquids with shorter alkyl chain substituent is better than that of ionic liquids with longer alkyl chain substituent. 	EMIM-Cl	1-ethyl-3-methylimidazolium chloride
	EMIM-Br	1-ethyl-3-methylimidazolium bromide
	PMIM-I	1-propyl-3-methylimidazolium iodide
	BMIM-Cl	1-butyl-3-methylimidazolium chloride
	BMIM-Br	1-butyl-3-methylimidazolium bromide
	BMIM-I	1-butyl-3-methylimidazolium iodide
3. Xiao-Sen Li, Yi-Jun Liu, Zhi-Yong Zeng, Zhao-Yang Chen, Gang Li, and Hui-Jie Wu.: Equilibrium Hydrate Formation Conditions for the Mixtures of Methane + Ionic Liquids + Water, A journal of Graduate University of Chinese Academy of Science, Beijing, P. R. China (2011). Analysis: <ul style="list-style-type: none"> Strong electrostatic charges and hydrogen bond with water, could shift the equilibrium hydrate dissociation/stability curve to a lower temperature and, at the same time, retard the hydrate formation by slowing down the hydrate nucleation rate 	MMIM-I	1,3-dimethyl-imidazolium iodide
	EMIM-I	1-ethyl-3-imidazolium iodide
	OH-C ₂ MIM-Cl	1-hydroxyethyl-3-methyl-imidazolium chloride
	N _{1,1,1,1} -Cl	Tetramethyl-ammonium chloride
	N _{1,1,1,1} OH-Cl	Hydroxyethyl-trimethyl-ammonium chloride
4. Tuning Ionic Liquids for hydrate inhibition, Volume 47, Issue 22, Pages 6341-6343, (14 JUNE 2011). Analysis: <ul style="list-style-type: none"> Special function group (oxygen, hydroxyl group), create intermolecular hydrogen bonding with hydroxyl group of water, resulting disruption at hydrogen bond between water molecules. Hydroxyethyl (HEMP) shows significant strong inhibitor's behaviour such as low concentration yet it has the longest induction time among all. HEMP also functions as thermodynamic inhibitor in theoretical terms; therefore, it is listed as a benchmark for future research. 	HEMP-BF ₄	1-hydroxyethyl-N-methyl pyrrolidinium tetrafluoroborate
	EMIM-BF ₄	1-ethyl-3-methylimidazolium tetrafluoroborate
	BMP-BF ₄	1-butyl-1-methylpyrrolidinium tetrafluoroborate

2.6 Info on CO₂ Hydrate Formation Experiment

Carbon dioxide has been known to be among a number of molecules that can form clathrate hydrate. Based on a study [11] carbon dioxide hydrate was classified as a

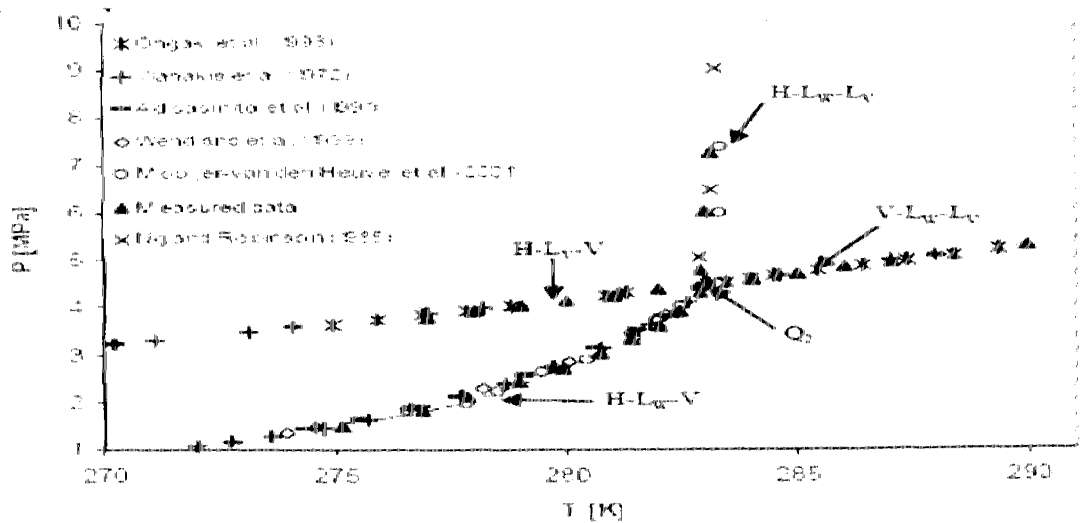


Figure 2.5: Three Phase Equilibrium Data for Carbon Dioxide and Water Hydrate System^[8]

As shown in this figure, the hydrate stability region is bounded by the H-I-V, H-LW-V and H-LW-LCO₂. As such, at any specified temperature, carbon dioxide hydrate will be stable as long as the pressure of the system is higher or equal to the equilibrium pressure of the system. Carbon dioxide hydrate has two quadruple points, Q1 and Q2. The quadruple point Q1 is a four-phase equilibrium point of I-Lw-H-V and it is located at 273.1 K and 1.256 MPa. The quadruple point Q2 is a fourphase equilibrium point of Lw-H-Lv-V and is located at 283.0 K and 4.499 MPa.

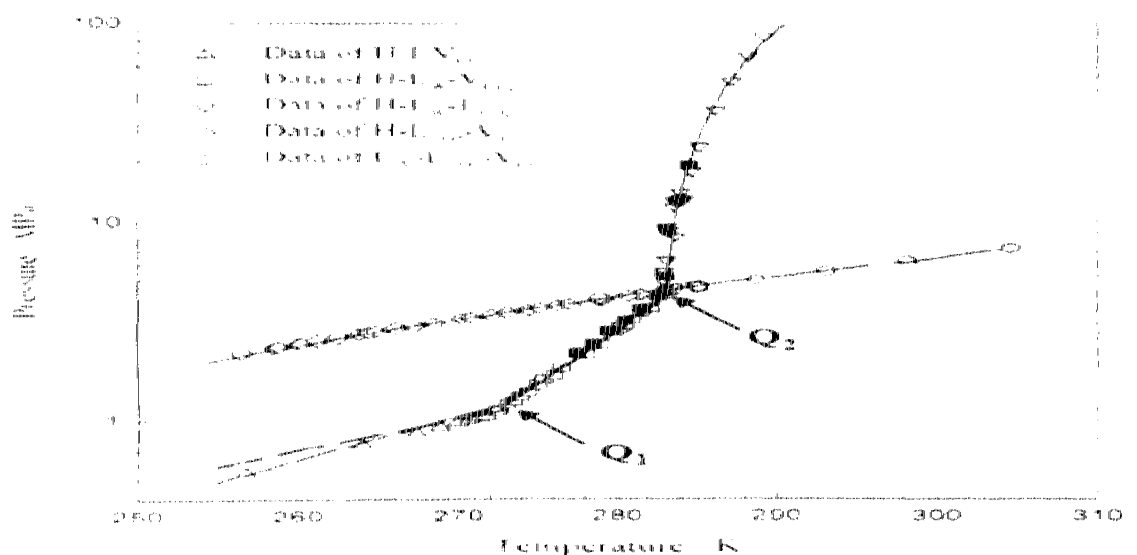


Figure 2.6: Three Phase Equilibrium Data for Carbon Dioxide Hydrate Formation^[8]

CHAPTER 3.0

METHODOLOGY

3.1 Chemical Identification

The chemical to be used in this work is presented in table 3.1

Table 3.1: Ionic liquid studied in this work

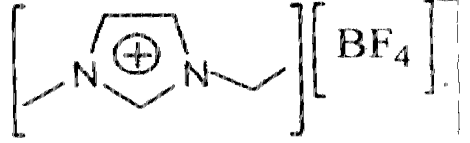
Symbol	Chemical name	Chemical structure
EMIM BF ₄	1-ethyl-3-methylimidazolium tetrafluoroborate	

Table 3.2: Materials involved with their suppliers and phases

Particular	Supplier	Phase
EMIM BF ₄	MERCK Sdn. Bhd.	Liquid (10ml)
Carbon Dioxide (CO ₂)	MOX-LINDE	Gas
Deionized Water (H ₂ O)	Own	Liquid

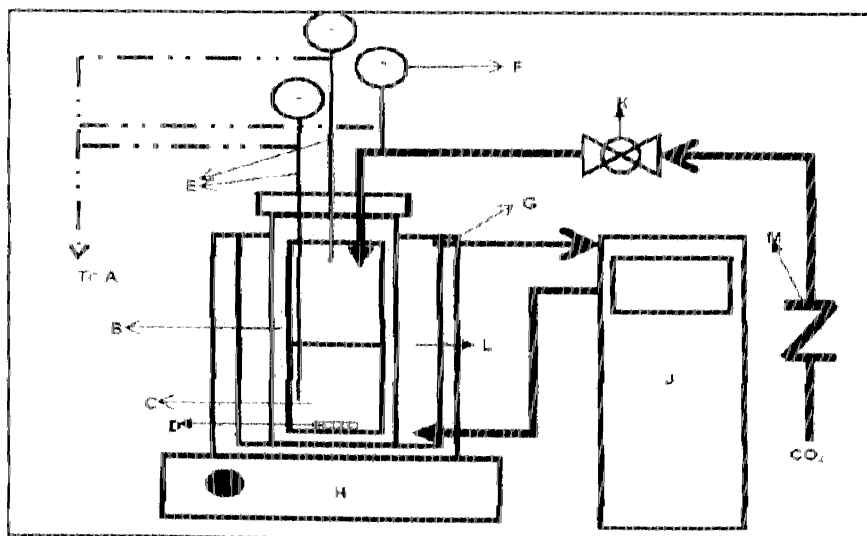
Assumption on experiment HPKM

First assumption is that the hydrate carbon dioxide remains stable at specified temperature, as long as the pressure of the system is higher or equal to the equilibrium pressure of the system. Second, the carbon dioxide hydrate formation is in first order reaction. The hydrate growth process is considered in the region from the turbidity point, at which the hydrate formation is noticeable based on the sharp pressure decrease until the stationary point. The amount of carbon dioxide gas dissolved in the liquid phase is not considered during hydrate growth because super saturation condition is maintained throughout the hydrate formation process. The hydrate particle formed are in the three phase equilibrium with the liquid and vapour phase.

3.2 Tools and Software Identification

Equipment name : High Pressure Kinetics Measurement (HPKM)
 Experiment setup time: 3-5hours
 Experiment duration : 2-3days

- i. HPKM system which consists of high pressure Cylindrical Cell Reactor (inner diameter of 4.55 cm, maximum workspace of 430ml, and maximum working pressure of 300MP



Labels:

- A: Data Acquisition System
- B: High Pressure Vessel
- C: Liquid Sample
- D: Stirrer
- E: Thermocouple
- F: Pressure Gauge
- G: Thermostatic Bath
- H: Magnetic Stirrer
- J: Cryostat
- K: Valve
- L: Thermostatic Liquid
- M: One way Valve^[11]

Figure 3.1: Schematic Illustration of the Apparatus for the High Pressure Kinetics Measurement (HPKM)^[8]

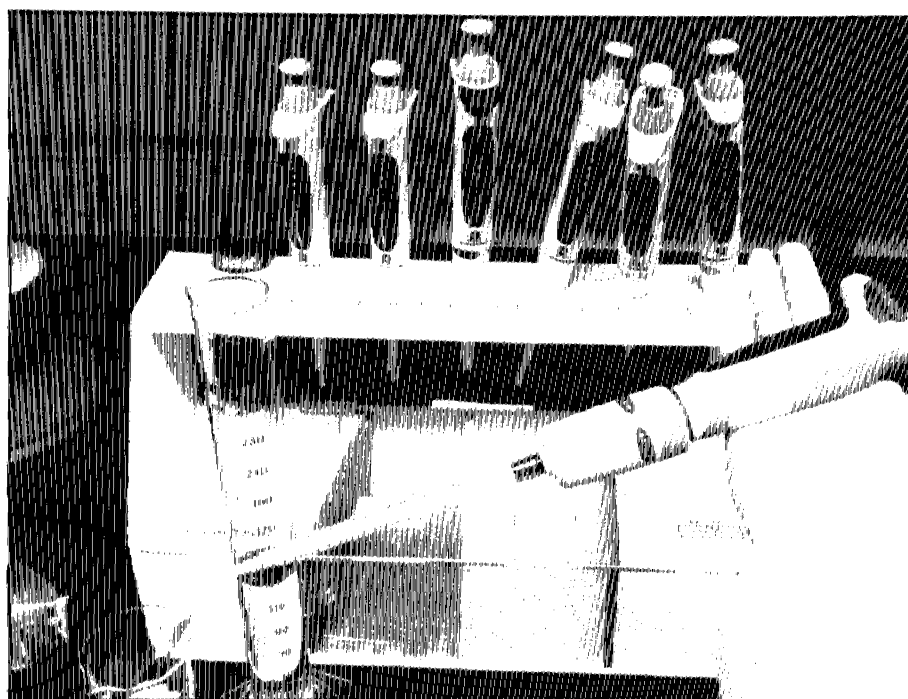


Figure 3.2: Micropipette used to acquire precise amount of liquid from Block 4 Level 1

3.3 Experiment Procedure for High Pressure Kinetics Measurement

1. First, 130 ml of deionized water and magnetic bar is inserted into the high pressure reactor. The bolt of the reactor is locked tightly to make sure there is no leakage.
2. In order to remove excess air inside the reactor, the reactor is purged with carbon dioxide gas 3-5 times. After that, the reactor is submerged inside the cooling bath.
3. The reactor is allowed to cool down at desired temperature and time was allowed to pass for the temperature to be stabilized. (Make sure that the temperature of the system is 2 K higher than the hydrate equilibrium temperature at specified pressure).
4. Next, sufficient carbon dioxide gas is introduced to the reactor up to desired experimental pressure. A decrease in pressure is observed. This is due to the dissolution of carbon dioxide in the liquid mixture.
5. When pressure regains stability, the temperature of the system is reduced to 5 K below the hydrate equilibrium temperature of the system.
6. When hydrate formation occurs, gas will be consumed, thus rapid pressure drop.
7. The change in pressure and temperature is recorded by data acquisition system.
8. When pressure of the system remains unchanged for 2 to 3 hour, this indicates that hydrate formation was considered complete and the experiment is ended.

Experiment Precaution

First, since the presence of other gases can lead to effects on temperature and pressure values at which hydrate will be formed, the type of hydrate formed and the occupation of hydrate cavities, the loading of carbon dioxide must be repeated 3 to 5 times to ensure that the concentration of other gases is kept at minimum level. Second, the system temperature must be above the equilibrium temperature of carbon dioxide hydrate formation (about 2 K higher). This is to avoid instant hydrate formation when loading of carbon dioxide take place. Another thing is to avoid parallax error while doing measurement and wrap the cooling bath with aluminium foil to prevent heat transfer from surrounding environment to the cooling bath.

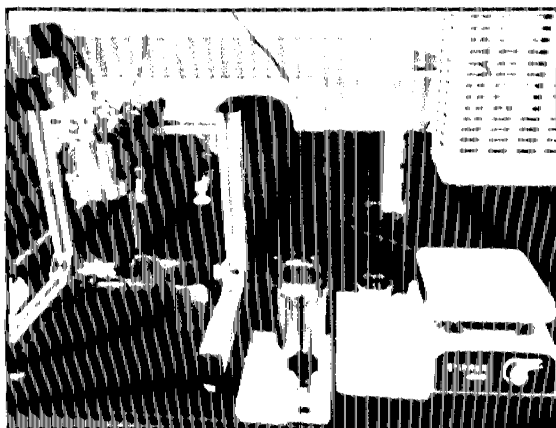


Figure 3.3: HPKM system with magnetic stirrer.

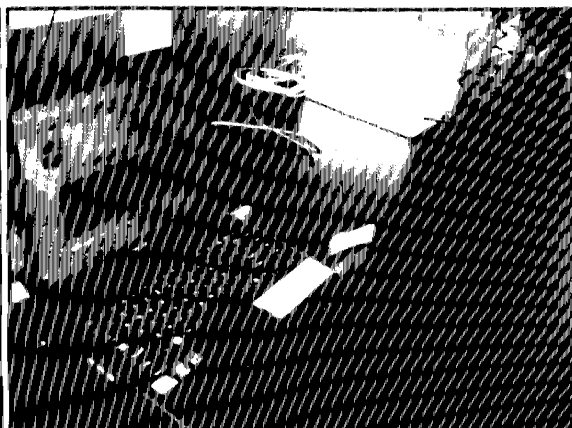


Figure 3.4: Computer + Data Acquisition System

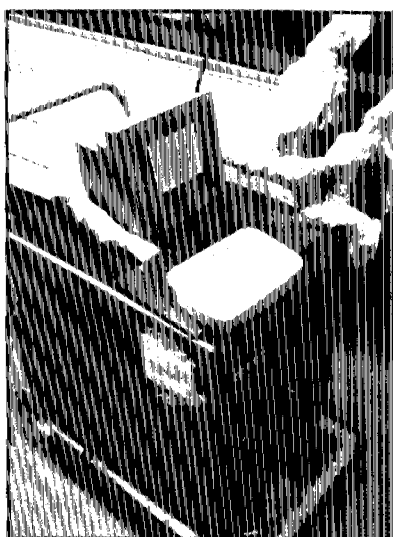


Figure 3.5: Cryostat (cooling device)

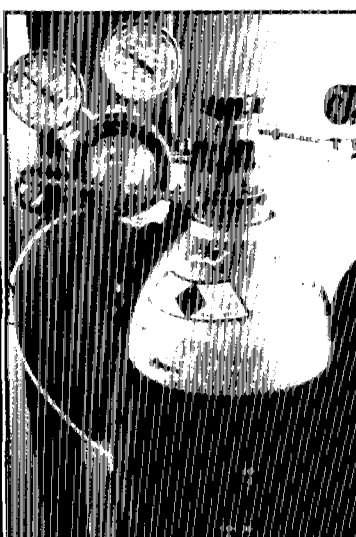


Figure 3.6: CO₂ gas tank



Figure 3.7: Reactor Submerged in Thermostatic Bath

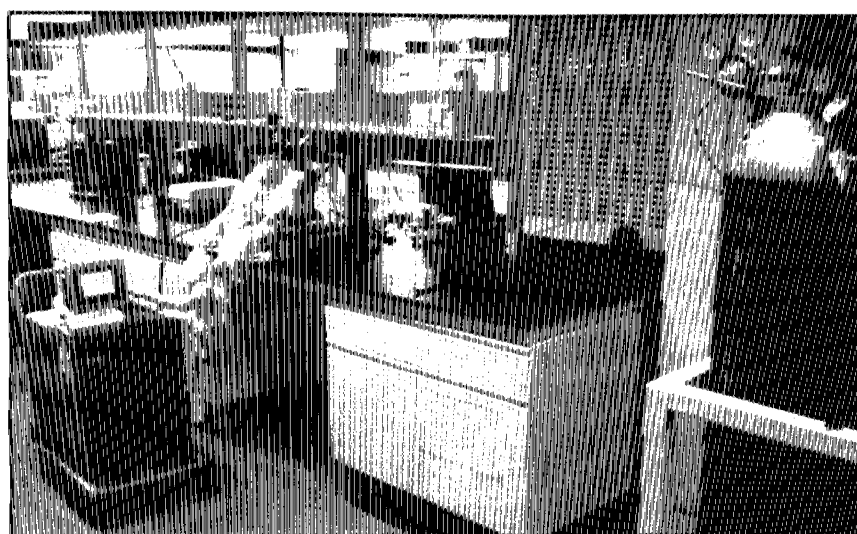


Figure 3.8: Experiments station at Block 5. 00. 01 laboratory

3.4 Research and Experiment Methodology

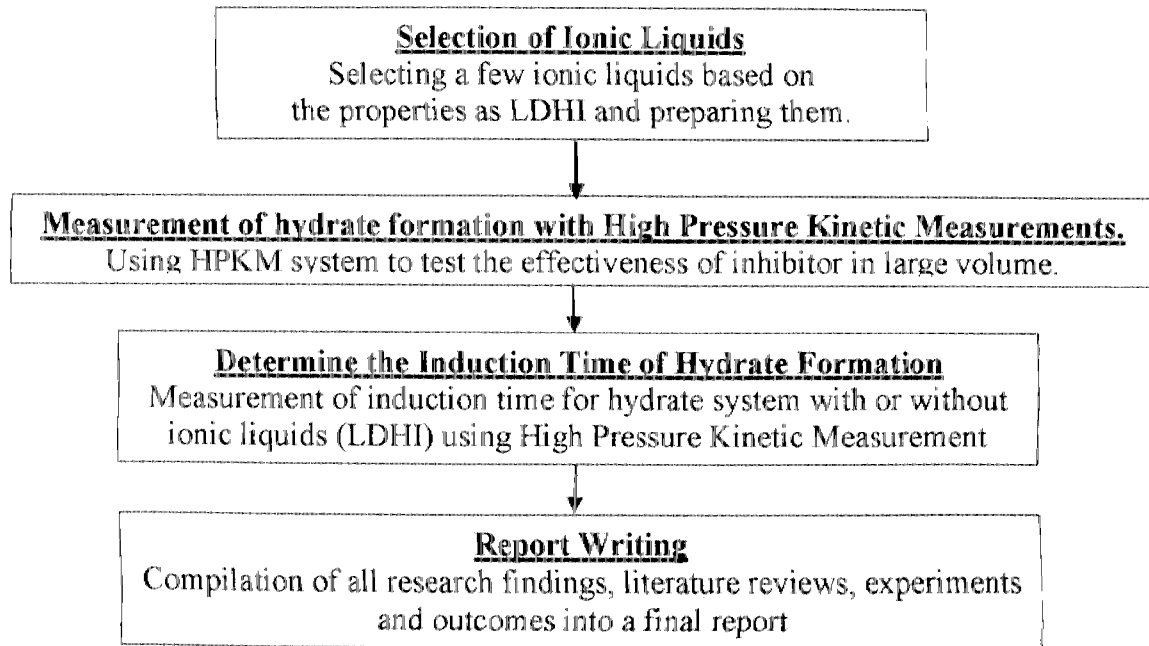


Figure 3.9: Flowchart of Research Methodology

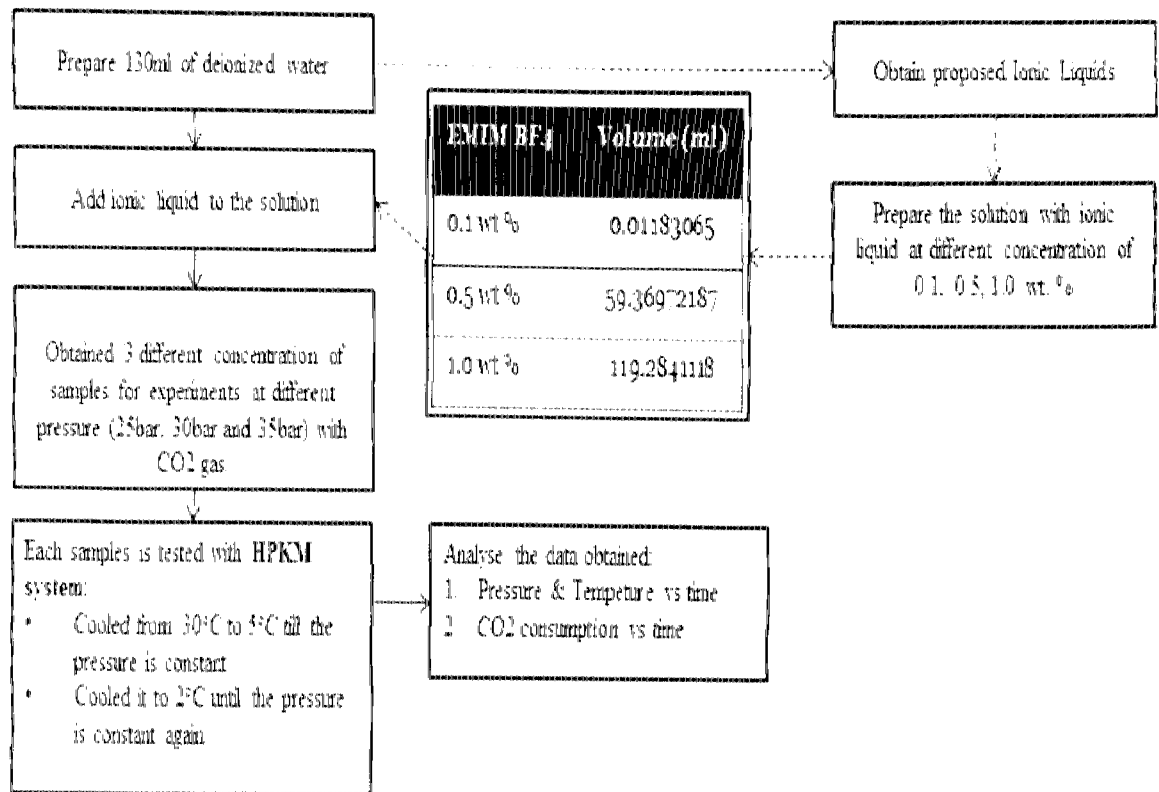


Figure 3.10: Flowchart of Experimental works

3.5 Project Activities

The research project will be run in four stages as described below:

i. Selection of ionic liquids

A systematic approach will be conducted by taking into account properties such as Chemical structure, toxicity, heat capacity, density, thermal conductivity, volatility, non-flammability, high thermal stability and the price of a group of ionic liquid.

ii. Measurement of hydrate formation with High Pressure Kinetic Measurement

For each one of the cycles, the high pressure vessel is loaded with a known volume and mass of a liquid sample. Then, the vessel is injected with gas until a desired pressure is achieved. Due to solubility of gas in the aqueous phase, the loading of the gas is conducted at initial temperature 2 K higher than the hydrate equilibrium temperature at a specified pressure.

Throughout the experimental work, a decrease of pressure should be observed during this step suggesting that the dissolution of gas in the aqueous mixture is taking place. When the pressure regains stability, the temperature of the system is slowly reduced to 5 K below the hydrate equilibrium temperature of the system. The temperature will be maintained above 273 K to prevent the formation of ice instead of the gas hydrate. When the desired final temperature condition is achieved, the system is left for 2 to 3 hours to ensure that the clathrate hydrate formation is completed. The system is allowed to reach equilibrium, normally in about 2-3 hours while the pressure and temperature data are collected by the data acquisition system.

iii. Determine the Induction Time of Hydrate Formation

The experimental work to gain information on the induction time will be conducted with High Pressure Kinetic Measurement. Data collected will be analysed and plotted into a graph.

iv. Report Writing

All data recorded during the experiments will be analysed and compiled together to prepare a final report. Useful information from journals, articles and any documents that were read and acquired are written down in the report and the FYP log book as well.

3.6 Example calculation for 1-Ethyl-3-methylimidazolium tetrafluoroborate, EMIM BF₄ at 0.1wt%

Basis of 100kg solution :

Mass of EMIM BF₄ = 0.1 kg
Mass of H₂O = 99.9 kg

Number of moles, n,	$= \frac{0.1 \text{ kg EMIM BF}_4}{197.97 \frac{\text{kg}}{\text{mol}}}$	Number of moles, n,	$= \frac{99.9 \text{ kg H}_2\text{O}}{18 \frac{\text{kg}}{\text{mol}}}$
for EMIM BF ₄	$= 5.051270395 \times 10^{-4}$	for H ₂ O	$= 5.55 \text{ k mol}$
	$= 0.505127039 \text{ mol}$		$= 5550 \text{ mol}$
Moles Fraction, ,	$= \frac{n \text{ EMIM BF}_4}{n \text{ EMIM BF}_4 + n \text{ H}_2\text{O}}$		
EMIM BF ₄	$= \frac{0.505127039 \text{ mol}}{0.505127039 \text{ mol} + 5550 \text{ mol}}$		
	$= 0.000091005$		
# Moles Fraction = Volume Fraction			
Therefore,			
Volume Fraction, χ	$= \frac{\text{Volume of EMIM BF}_4}{\text{Volume of H}_2\text{O}}$		
Volume of EMIM BF ₄ = Volume of H ₂ O \times χ value of EMIM BF ₄			
	$= 130 \text{ ml} \times 0.000091005$		
	$= 0.01183065 \text{ ml}$		
	$= 11.83 \mu\text{l}$		

****Please view Appendix 3 - Volume calculation for 1-Ethyl-3-methylimidazolium tetrafluoroborate, EMIM BF₄ at different concentrations (0.1wt%, 0.5wt% and 1.0wt%)**

3.7 Gantt Chart for FYP 2

Table 3.3: Gantt chart for the Second Semester Project Implementation

Detail/ Week	Sept		Oct 2011			Nov 2011							Dec 2011			Jan 2012	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15		
Continue Experiment with HPKM with LDHI- ionic liquids at concentration (0.1 wt%, 0.5 wt% & 1.0 wt %)																	
FYP 2 Log Book Recording																	
Submission of Progress Report										○							
Experiment with DSC @ high pressure (with and without LDHI)																	
Report Preparation																	
Pre-SEIDEX (Poster)											○						
Submission of Draft Report												○					
Submission of Dissertation & Technical Paper													○				
Oral Presentation														○			
Submission of Project Dissertation (Hard Bound)															○		

3.6 Key Milestones and Dates

- Completion of Progress Report
 - Completion of Poster
 - Completion of Dissertation & Technical Paper
 - Submission of Project Dissertation
 - Oral Presentation
- 25th November 2011
 9th December 2011
 23th December 2011
 4th January 2012
 16th January 2012

CHAPTER 4.0

RESULT AND DISCUSSION

4.1 Experiments status and example of CO₂ hydrates

Table 4.1: Experiments start date.

Experiments	25bar	30bar	35bar
Without EMIM BF ₄	10 th Nov	2 nd Dec	22 nd Nov
With 0.1wt % EMIM BF ₄	13 th Nov	5 th Dec	25 th Nov
With 0.5wt % EMIM BF ₄	17 th Nov	10 th Dec	27 th Nov
With 1.0wt % EMIM BF ₄	19 th Nov	14 th Dec	30 th Nov
With 10.0wt% EMIM BF ₄	-	29 th Dec	-

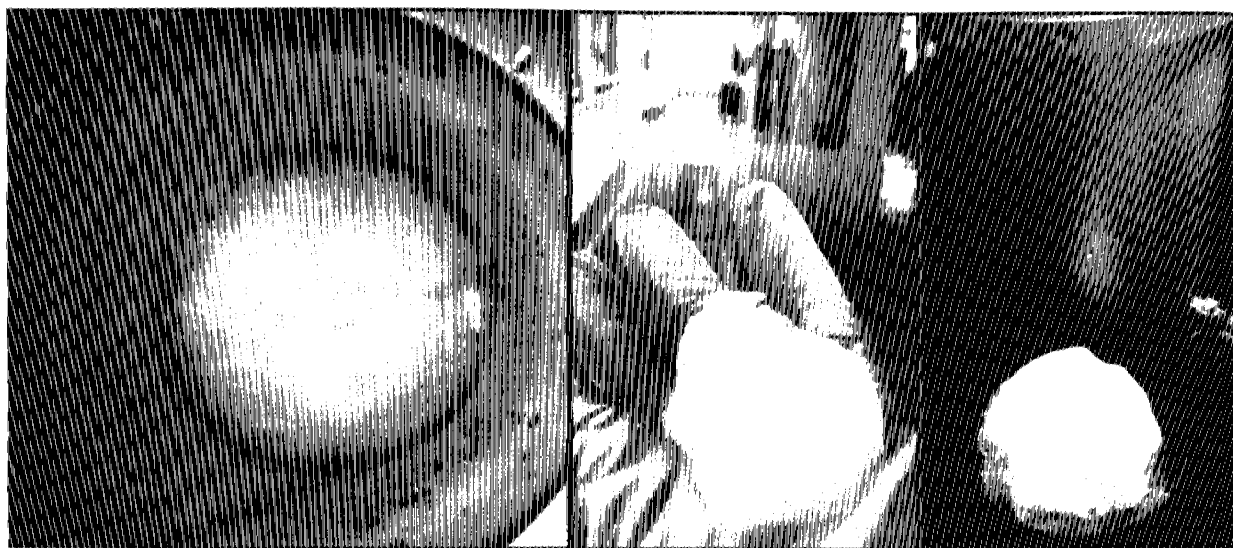


Figure 4.1: Example of CO₂ hydrate formation in reactor @ 30bar

Figure 4.2: CO₂ hydrate formation outside of reactor @ 30bar

Figure 4.3: CO₂ hydrate formation outside of reactor @ 30bar

4.2 Results

4.2.1 Data Analysis for experiments at pressure, 25bar and temperature, 2 °C

Without Ionic Liquid @25bar

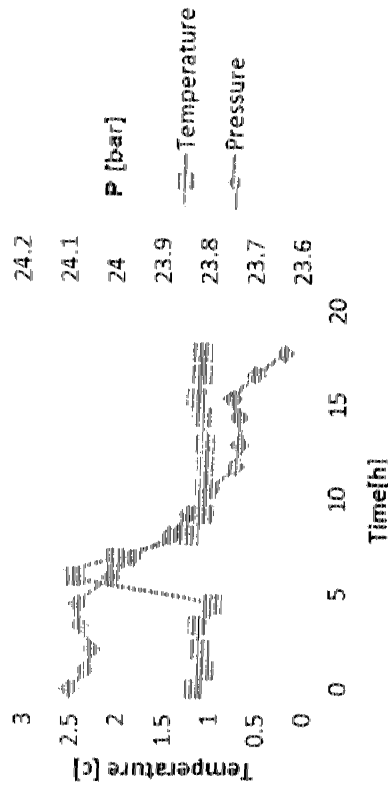


Figure 4.4: Without Ionic Liquid @ 25bar

0.5wt %EMIM BF₄ @ 25bar

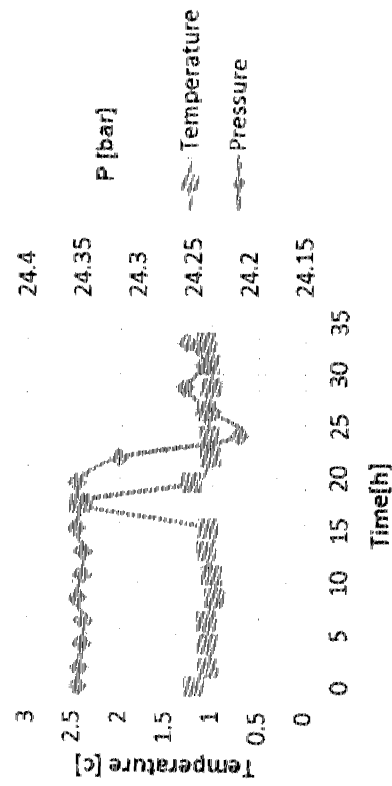


Figure 4.6: With 0.5wt% EMIM BF₄ @ 25bar

0.1wt% EMIM BF₄ @ 25bar

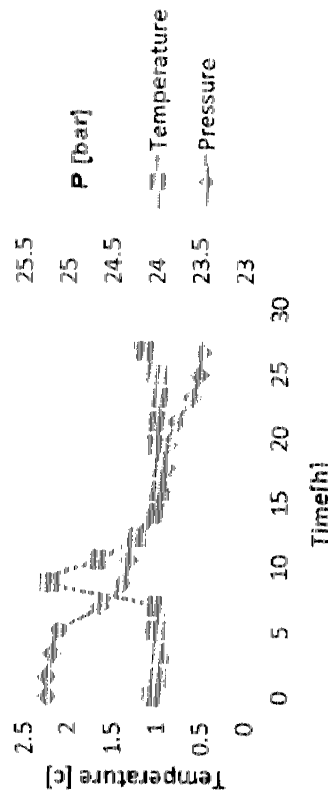


Figure 4.5: With 0.1wt% EMIM BF₄ @ 25bar

1.0wt %EMIM BF₄ @ 25bar

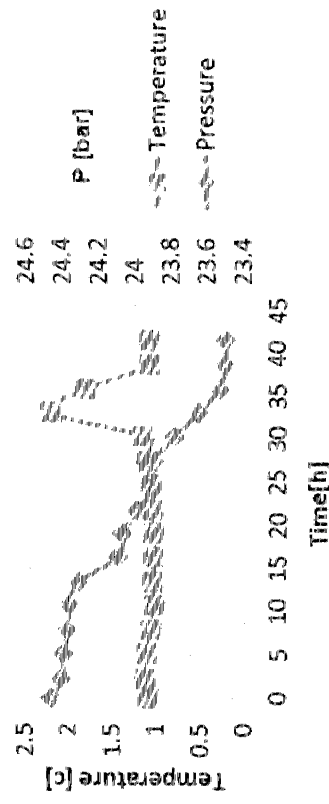


Figure 4.7: With 1.0wt% EMIM BF₄ @ 25bar

CO2 Hydrate Temperature VS Time @ 25bar

Without ILs
 0.1 wt%
 0.5 wt%
 1.0 wt%

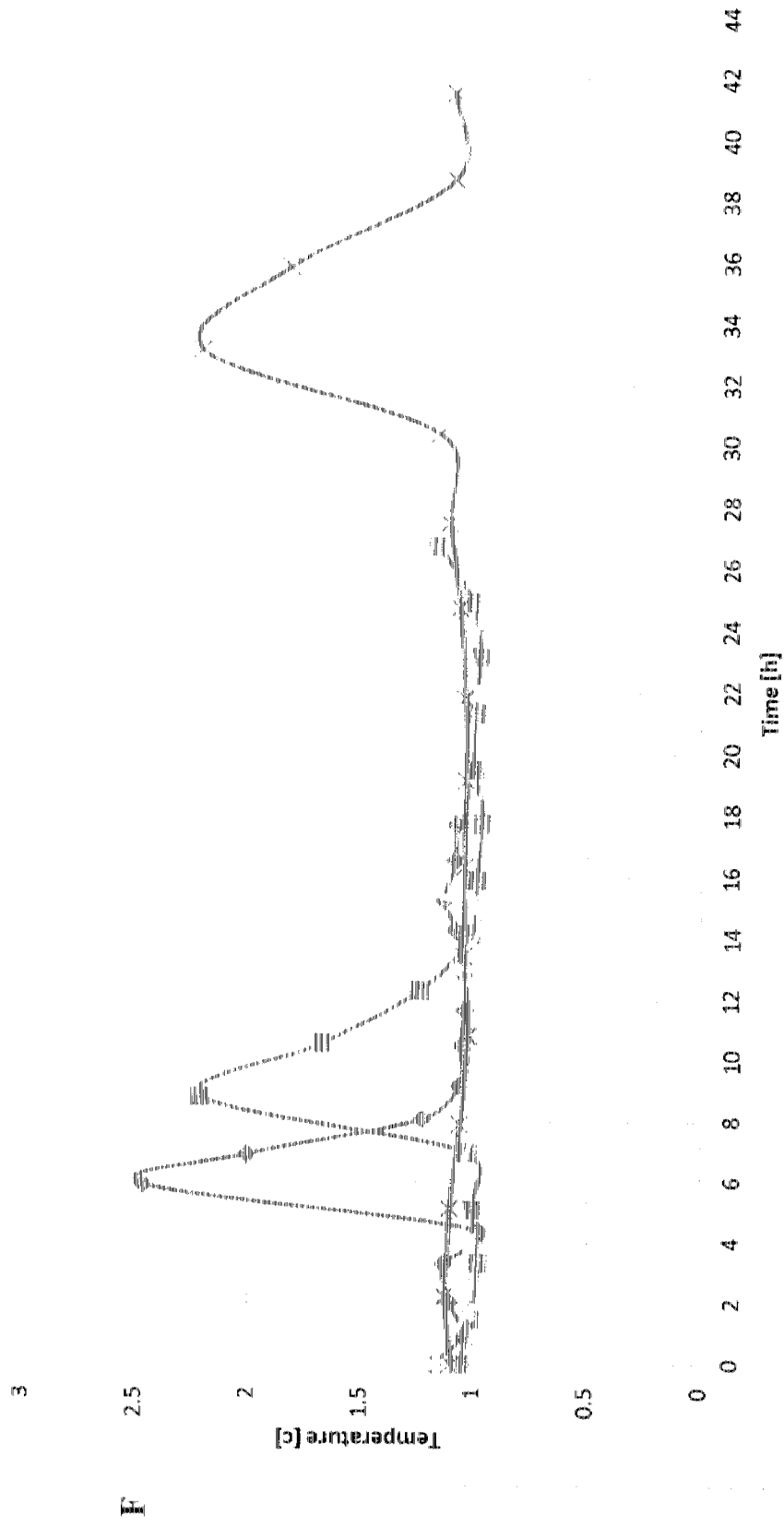


Figure 4.8: CO₂ Hydrate Temperature VS Time @ 25bar

CO₂ Hydrate Pressure VS Time @ 25bar

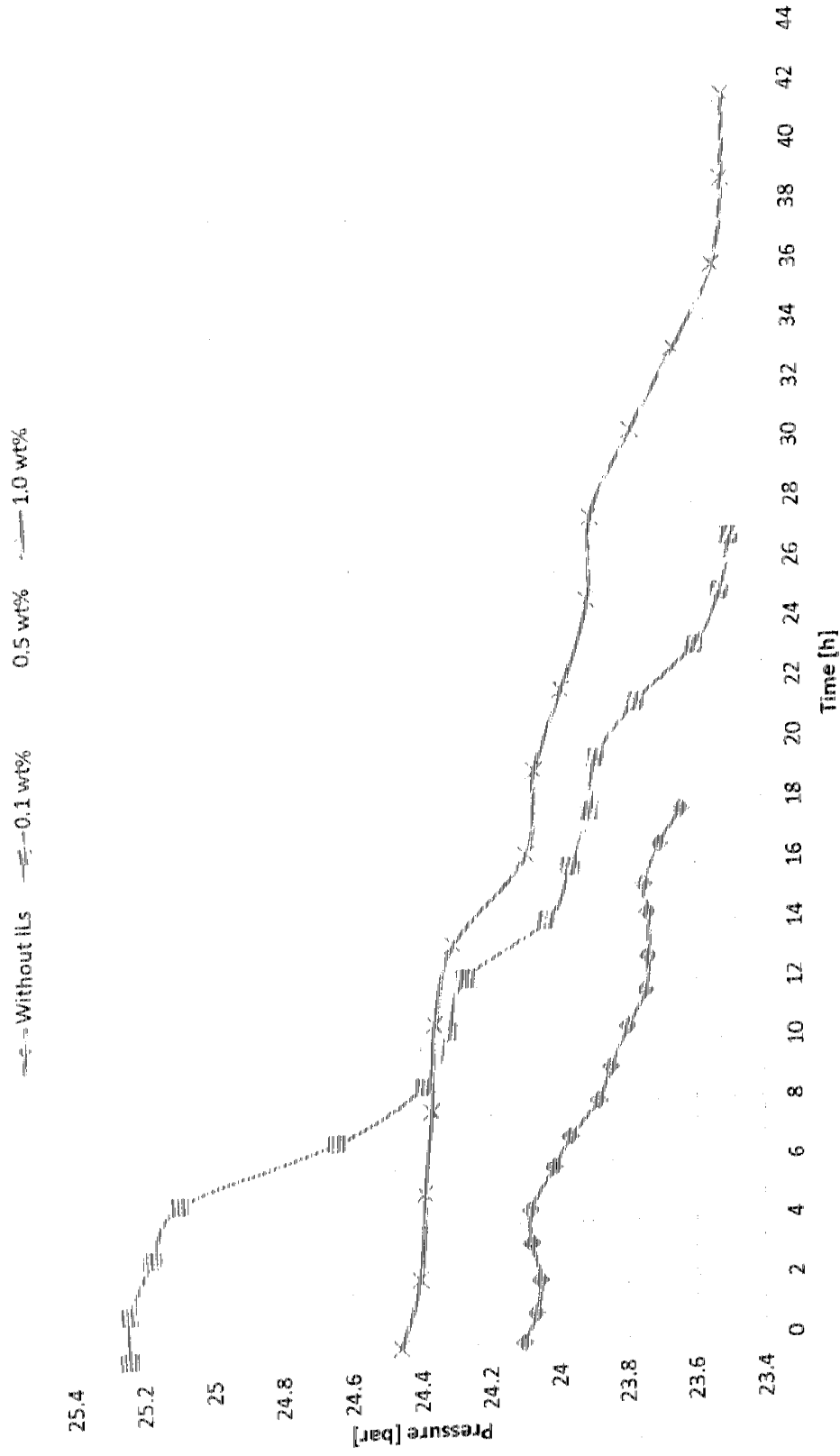


Figure 4.9: CO₂ Hydrate Pressure VS Time @ 25bar

4.2.2 Data Analysis for experiments at pressure, 30bar and temperature, 2 °C

Without Ionic Liquid @ 30bar

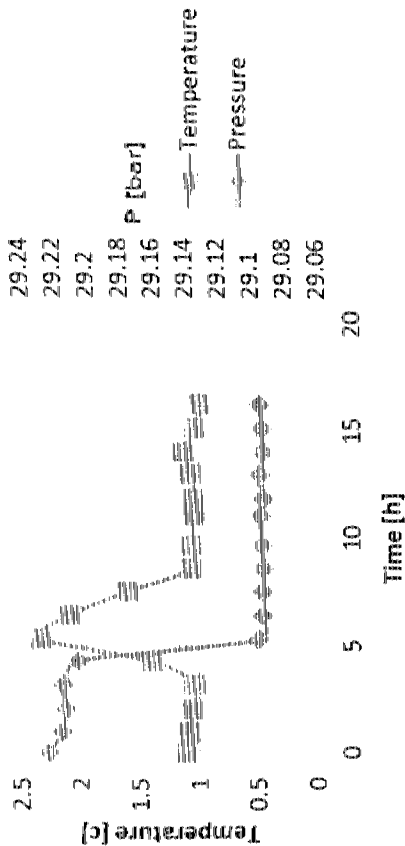


Figure 4.10: Without Ionic Liquid @ 30bar

0.1wt %EMIM BF₄ @30bar

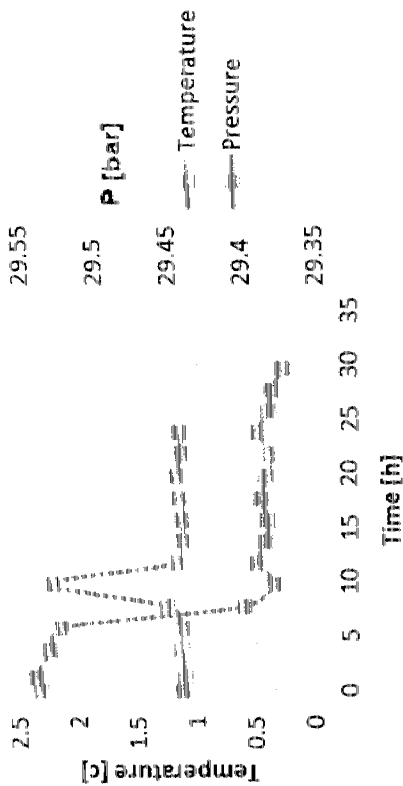


Figure 4.11: With 0.1wt% EMIM BF₄ @ 30bar

0.5wt %EMIM BF₄ @30bar

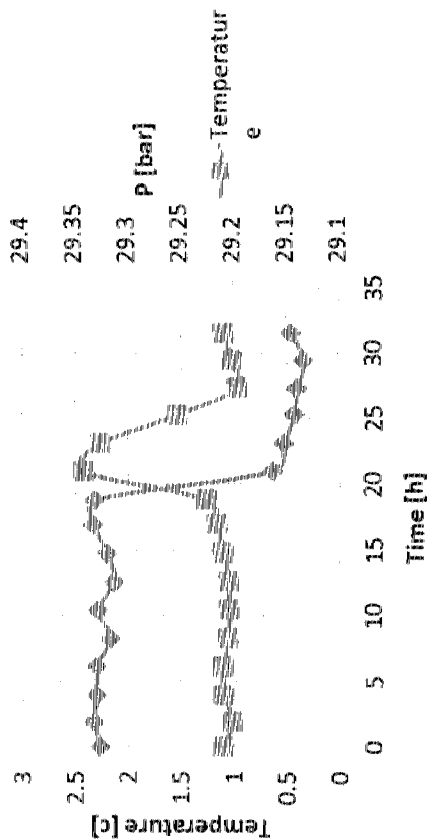


Figure 4.12: With 0.5wt% EMIM BF₄ @ 30bar

1.0wt %EMIM BF₄ @ 30bar

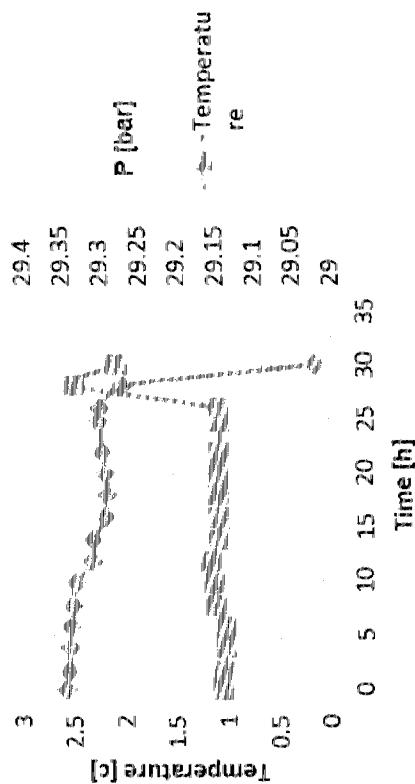


Figure 4.13: With 1.0wt% EMIM BF₄ @ 30bar

CO2 Hydrate Temperature VS Time @ 30bar

Without ILS 0.1 wt% 0.5 wt% 1.0 wt%

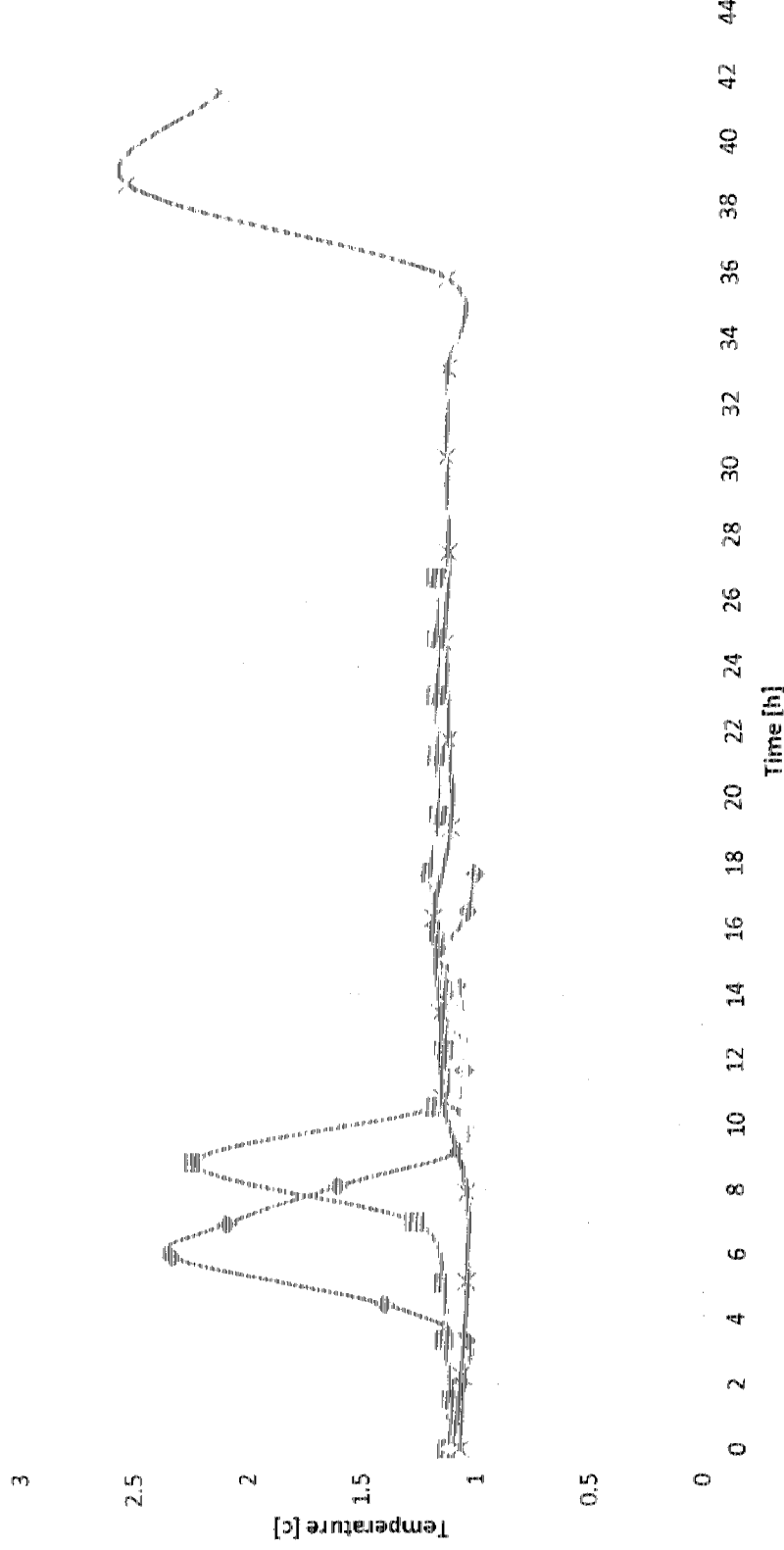


Figure 4.14: CO₂ Hydrate Temperature VS Time @ 30bar

CO2 Hydrate Pressure VS Time @ 30bar

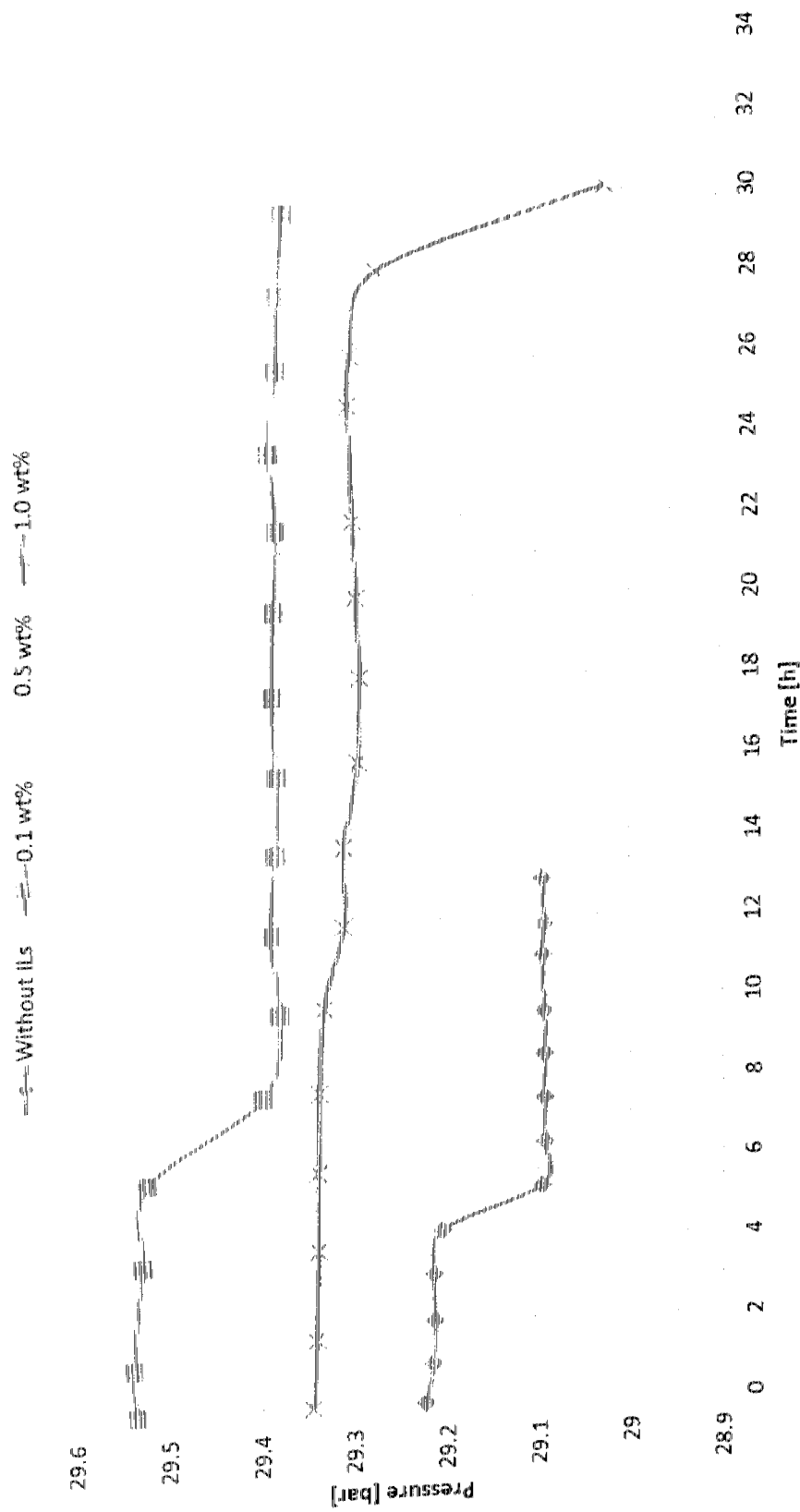


Figure 4.15: CO₂ Hydrate Pressure VS Time @ 30bar

4.2.3 Data Analysis for experiments at pressure, 35bar and temperature, 2 °C

Without Ionic Liquid @ 35bar

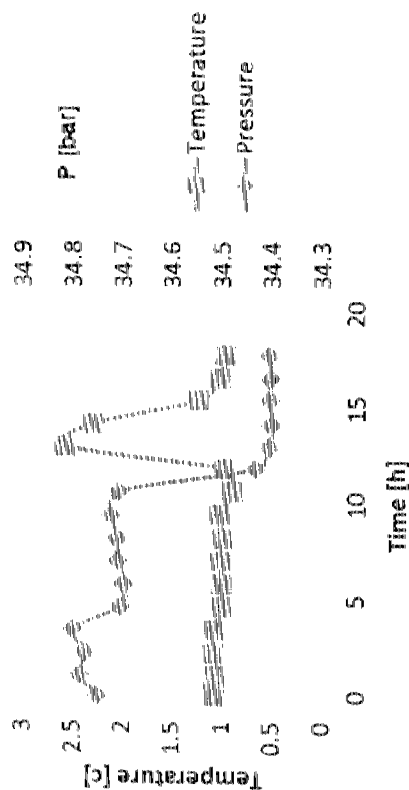


Figure 4.16: Without Ionic Liquid @ 35bar

0.1wt %EMIM BF₄ @35bar

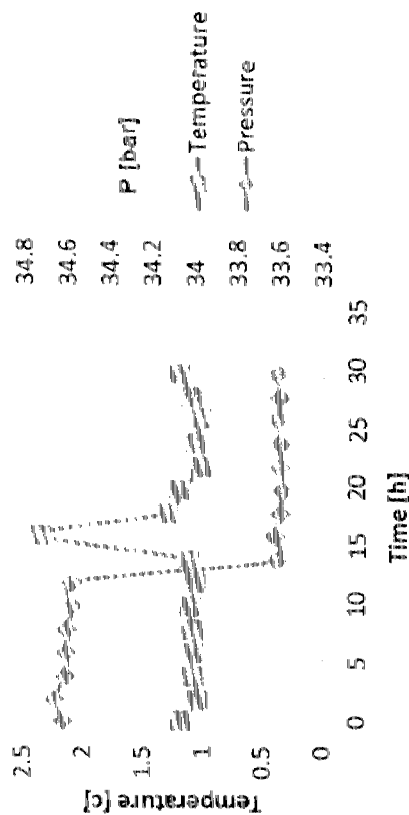


Figure 4.17: With 0.1wt% EMIM BF₄ @ 35bar

0.5wt %EMIM BF₄ @ 35bar

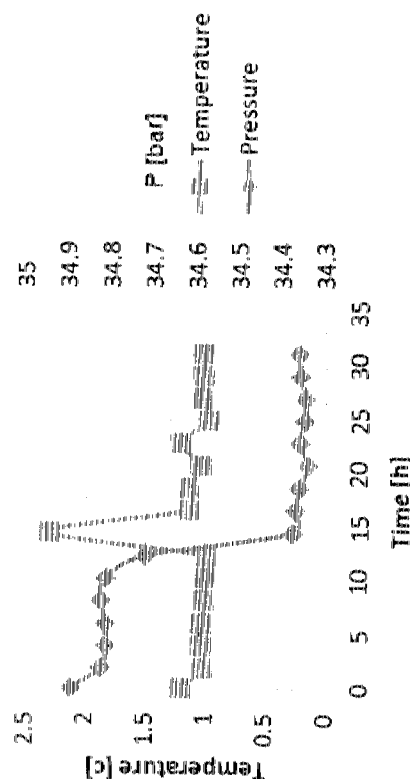


Figure 4.18: With 0.5wt% EMIM BF₄ @ 35bar

1.0wt %EMIM BF₄ @ 35bar

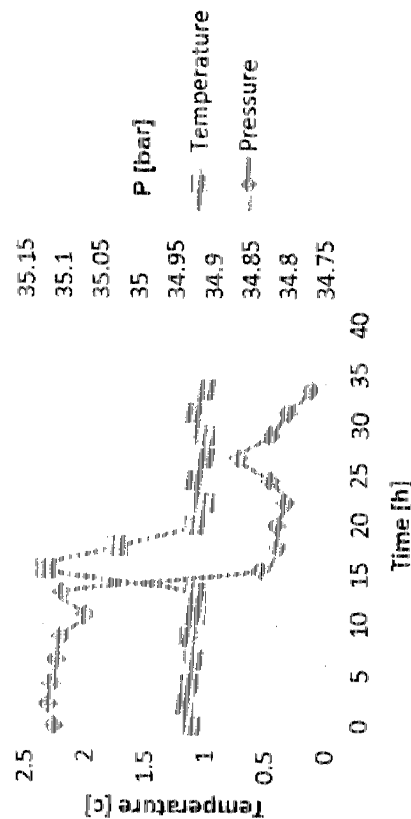


Figure 4.19: With 1.0wt% EMIM BF₄ @ 35bar

CO2 Hydrate Temperature VS Time @ 35bar

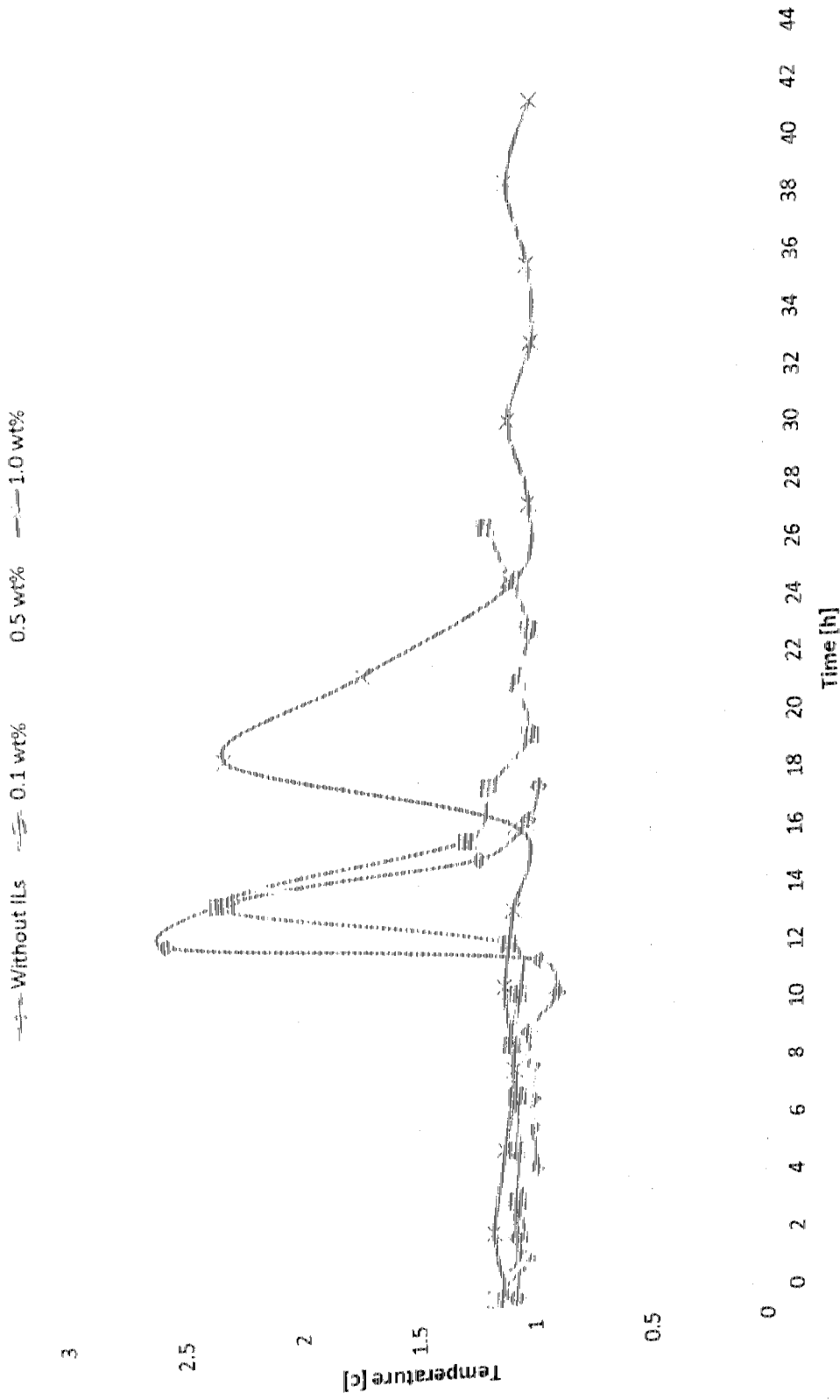


Figure 4.20: CO₂ Hydrate Temperature VS Time @ 35bar

Pressure VS Time @ 35bar

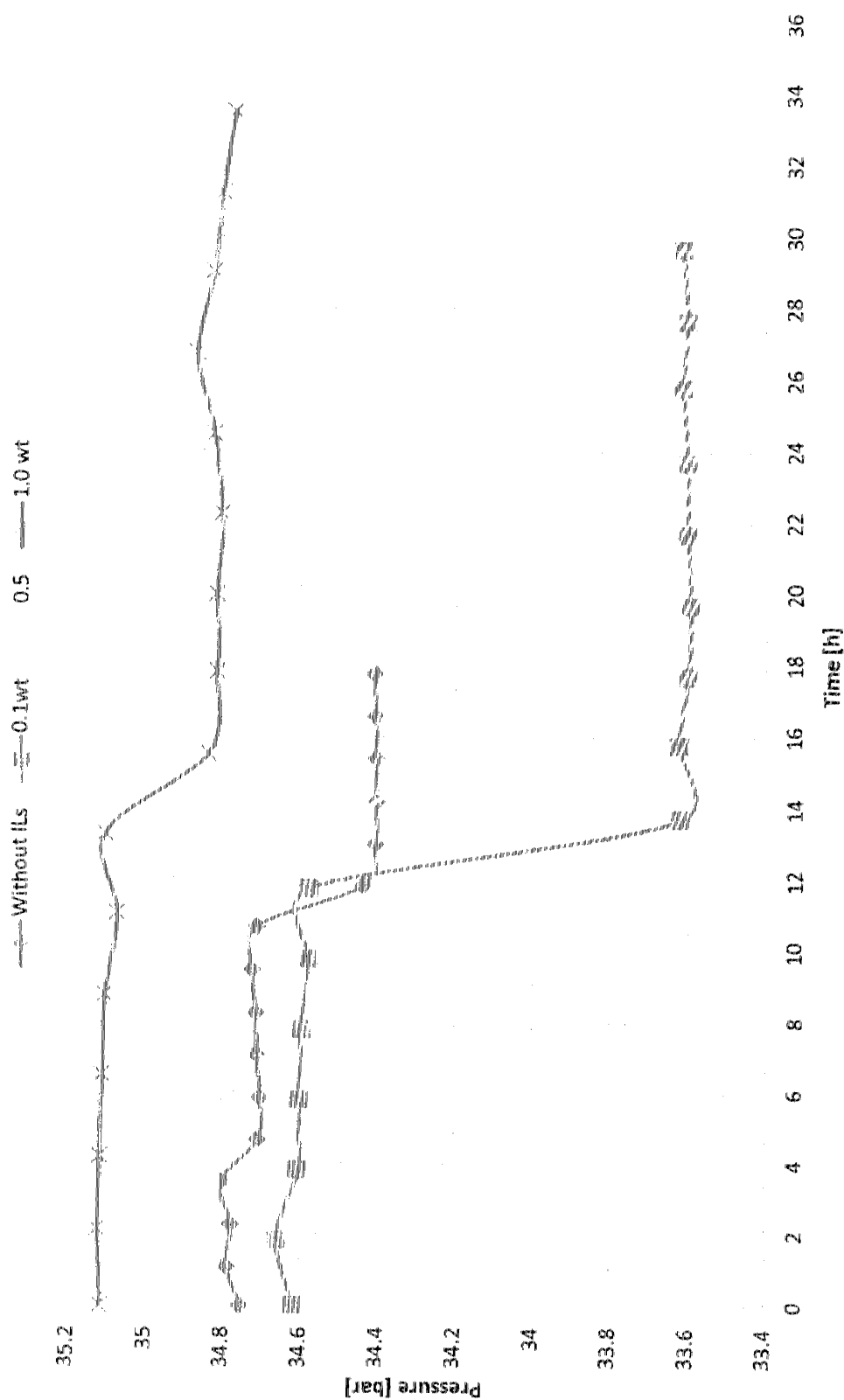


Figure 4.21: CO₂ Hydrate Pressure VS Time @ 35bar

4.3 Discussion

The induction time is an important indicator to characterize the kinetics of gas hydrate crystallization. The induction time is the time elapsed until the moment at which the onset of precipitation can be detected, which is the sum of the time for critical nucleus formation and growth to detectable size.^[1] For heterogeneous nucleation, the nucleation rate depends on many factors, such as the cell wall roughness and the presence of impurities and particles in the sample, including the driving force.

Isothermal mode experiments at 2°C and pressure at 25bar, 30bar and 35bar are performed to study the induction time. Experiment with concentrations of 10.0 wt% of EMIM BF₄ is also used in these isothermal run at 30bar only.

From temperature and pressure profile, we can see a rapid increase of temperature to a maximum point because hydrate formation is an exothermic process (In thermodynamics, the term exothermic ("outside heating") describes a process or reaction that releases energy from the system, form of heat release). Meanwhile, the pressure decreases tremendously as gas is consumed during the hydrate formation process until it reaches the point where no more hydrate forms, then the pressure becomes almost constant again.

Kinetic inhibitors are typically used at concentrations of 1 wt% or less. Examples of Temperature and Pressure VS Time graph for each experiments are shown, demonstrating that the CO₂ hydrate formation can be prolonged due to the presence of ionic liquid as inhibitors. Most of the experiments showed the effect of ionic liquid towards the CO₂ hydrate formation. As we can see from the data records, 0.1 wt% of EMIM BF₄ has the least effect on the hydrate formation while the effect can be tracked as we increase the concentration to 0.5 wt% and 1.0 wt%.

4.4 Results on the induction time for all pressures and concentrations

Table 4.2: Induction time of Carbon Dioxide hydrate Formation at various pressures

Samples	Range of induction time (hour)		
	25bar	30bar	35bar
Pure Deionized Water	3.1	3.5	11.5
0.1 wt% [EMIM] [BF ₄]	6.3	6.0	13.2
0.5 wt% [EMIM] [BF ₄]	16.1	20.0	14.6
1.0 wt% [EMIM] [BF ₄]	30.2	36.3	17.1

wt%: weight percentage of inhibitors. Temperature=275K

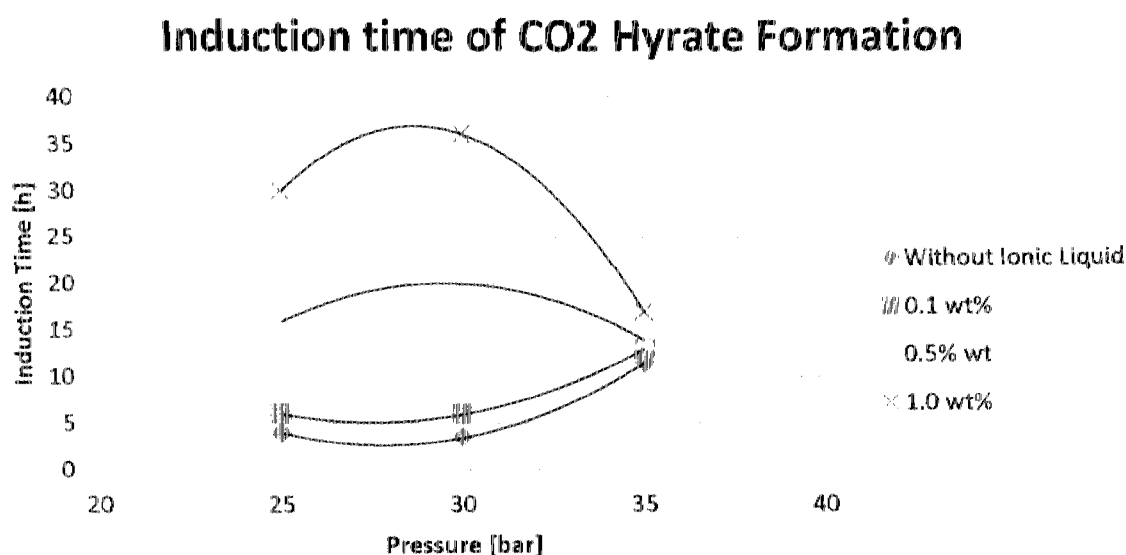


Figure 4.22: Induction VS Pressure for CO₂ Hydrate Formation

Induction time of CO₂ Hydrate Formation

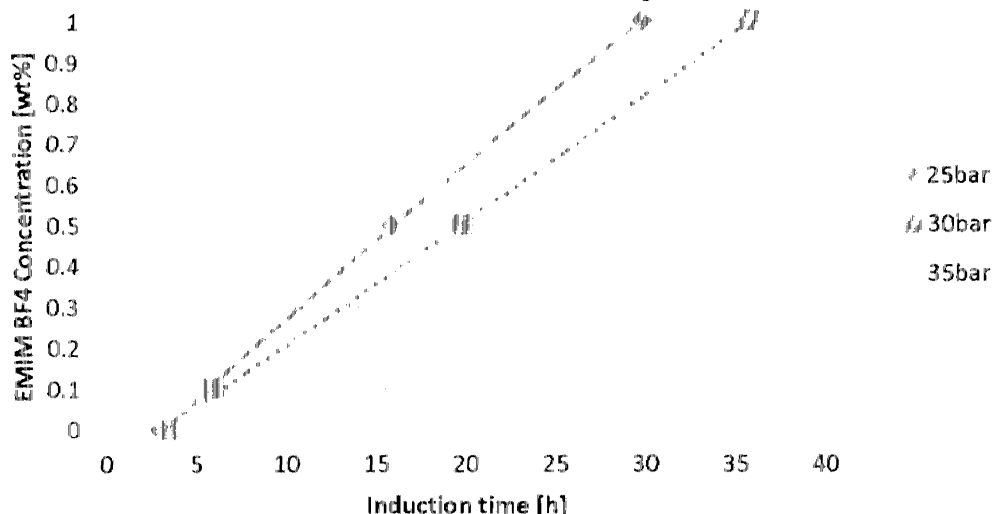


Figure 4.23: Concentration VS Induction time for CO₂ Hydrate Formation

4.5 Data Analysis for additional experiment (10.0 wt% concentration) at pressure, 30bar and temperature, 2 °C

It is of interest to test if the ILs can function as thermodynamic inhibitors (THIs) with the concentration at 10.0 wt%. Thermodynamic inhibitors are usually used at a concentration of 10.0 wt% or more while the kinetic inhibitors are usually used at a concentration of 1 wt% or less.

10.0wt %EMIM BF₄ @ 30bar

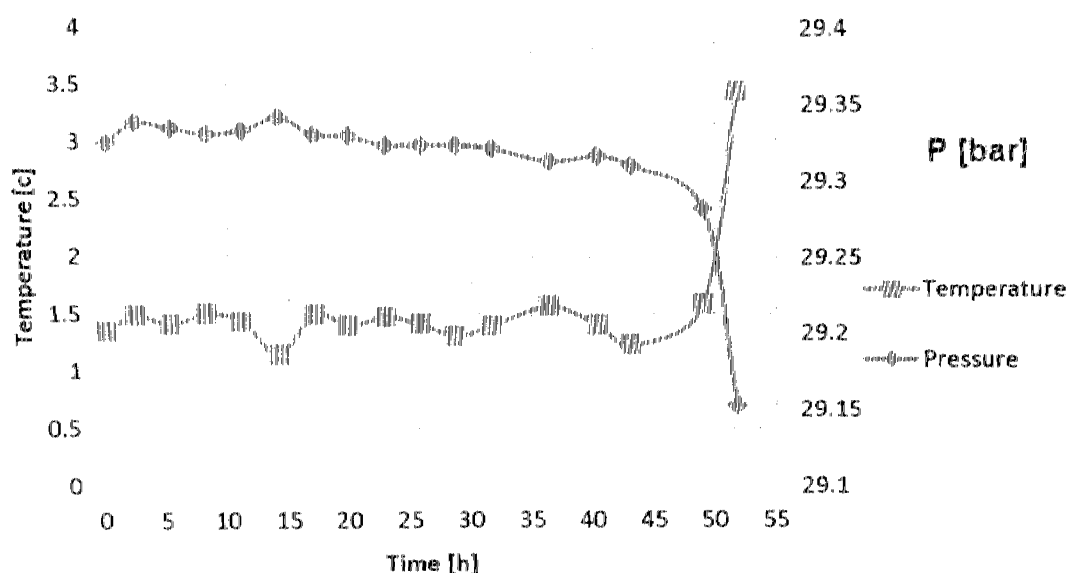


Figure 4.24: With 10.0 wt% EMIM BF₄

CO2 Hydrate Pressure VS Time @ 30bar

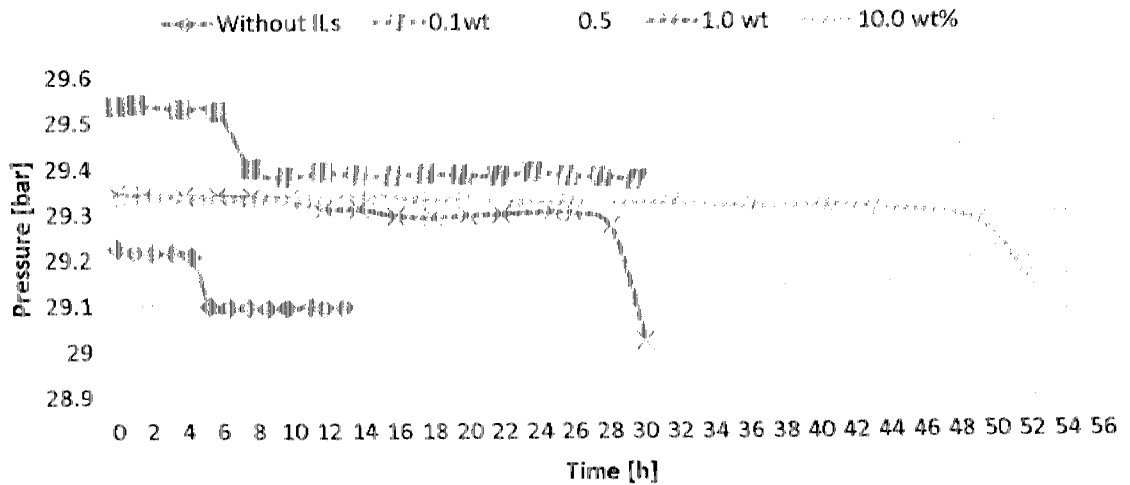


Figure 4.25: CO2 Hydrate Pressure VS Time (including 10 wt%)

CO2 Hydrate Temperature VS Time @ 30bar

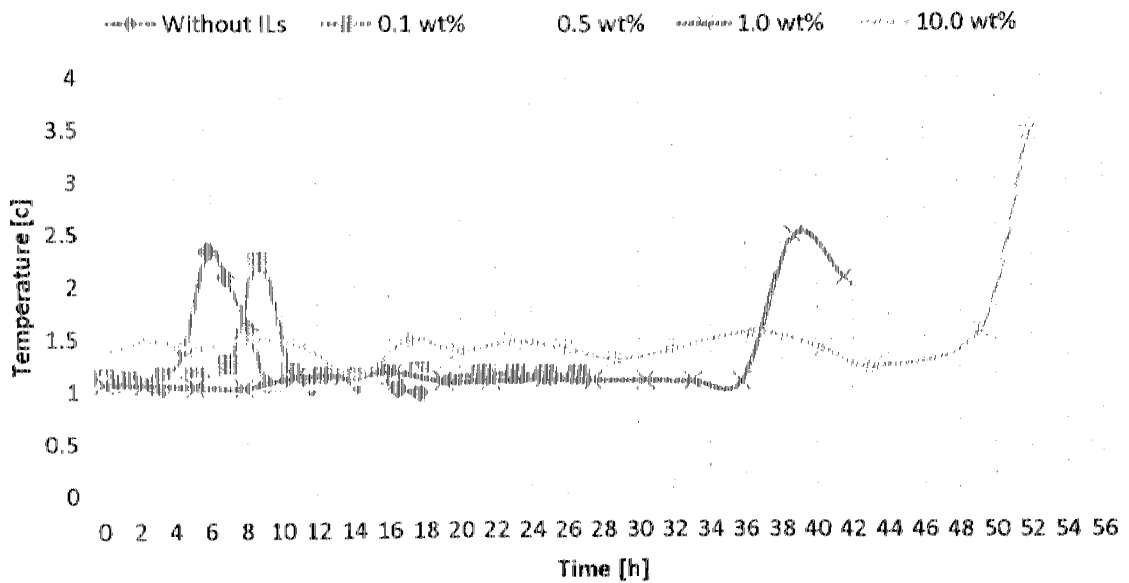


Figure 4.26: CO2 Hydrate Temperature VS Time (including 10 wt%)

Since the induction time of the sample containing 10.0 wt% EMIM BF₄ is the longest, the data is compared with the other experiments' results at different concentrations with specific pressure. Based on the experiments done for CO₂ Hydrate, the graphs above show that higher concentration of EMIM BF₄ increases the induction time, which is desirable.

The result for 10 wt% concentration of EMIM BF₄ towards CO₂ Hydrate is the difference in induction time when 10% EMIM BF₄ is used to inhibit the formation of CO₂ Hydrate is small. Thus, higher concentration such as more than 10 wt% doesn't have the great effect as a thermodynamic inhibitor.

Table 4.3: Induction time of Carbon Dioxide hydrate Formation at various pressures

Samples	Range of induction time (hour)		
	25bar	30bar	35bar
Pure Deionized Water	3.1	3.5	11.5
0.1 wt% [EMIM] [BF ₄]	6.3	6.0	13.2
0.5 wt% [EMIM] [BF ₄]	16.1	20.0	14.6
1.0 wt% [EMIM] [BF ₄]	30.2	36.3	17.1
10.0 wt% [EMIM] [BF ₄]	-	48.0	-

wt%: weight percentage of inhibitors. Temperature=275K

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Based on the preliminary study done, the following conclusions can be made:

- A fundamental knowledge on formation of gas hydrates within the hydrate formation region at low temperature and high pressure condition was built.
- Experiments were conducted with various concentration (0.1 wt%, 0.5 wt%, 1.0 wt% and 10.0 wt%) of ionic liquid at different pressure (25bar, 30bar and 35bar).
- A better understanding on Ionic Liquids as LDHI has been achieved.

For the result, the induction time of CO₂ hydrate formation at 25bar from samples containing 0.1 wt% is about 6hours, 0.5 wt% is about 16hours and 1.0 wt% is about 30hours. While for experiments at 30bar, the induction time for concentration at 0.1wt% is about 6hours, 0.5 wt% is about 20hours, 1.0 wt% is about 36hours and 10.0 wt% is about 50hours. Lastly for experiment at 35bar, the induction time for concentration at 0.1 wt% is 13hours, 0.5 wt% at 14hours and 1.0 wt% is about 17hours.

Through the experiments, the learning of hydrate behaviour condition and the driving force based on the CO₂ phase equilibrium is important to determine the starting time for data recording. KHI retards gas hydrate formation and elongates the induction time at low dosages of 1 wt%.

The study of the effect of concentration on induction time shows that with higher concentration than 1 wt% such as 10 wt%, does not have much difference in retarding the hydrate formation as well as the total prices for purchasing the ILs.

In general, the development of ionic liquids as low dosage hydrate inhibitor (LDHI) can reduce the amount of chemical used for conventional hydrate inhibition method in pipeline. In addition, the environment impact will be reduced since ionic liquid is known as a green technology chemical. As a result, it will save up lots of operation cost (CAPEX & OPEX) and reduce safety hazards.

5.2 Recommendation for Future Works Expansion and Continuation

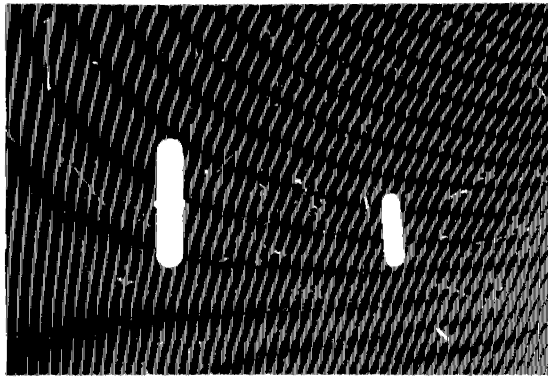


Figure 5.1: 2 different sizes of magnetic stirrers.



Figure 5.2: Difficulties to place both thermostatic bath and magnetic stirrer plate below the reactor.

- Use a bigger stirrer to create stronger stirring force (vibration) in the sample as hydrate formation rate will be faster. An alternative stirrer option will be the vertical stirrer which is the best mixing method for hydrate formation experiment. (Figure 5.1)
- Use less amount of liquid to make sure the whole medium is exposed instead of only the surface of the liquid.
- Calibration for the thermocouple needed to be done since there is some error with the temperature readings.
- A lower height of magnetic stirrer plate should be considered for the ease of setting up the HPKM system during experiment or manufacture a proper lift up jig for the reactor so that both thermostatic bath and magnetic stirrer plate can be placed below it. (Figure 5.2)
- System will be carried on with various class and type of ionic liquids as LDHI.
- Experiments should be conducted at higher pressure range from 70-150bar for a faster hydrate formation rate.
- Create a cover (thermal insulator) on top of thermostatic bath in order to reduce any heat loss or unwanted heat transfer with the surrounding air or a much proper thermostatic bath medium instead of plastic container.
- Future experiment can be done with High Pressure Differential Scanning Calorimeter (DSC) which is more precise in data recording for data comparison.

REFERENCES

- [1] Adisasmito, S., Frank, R.J., & Sloan, E.D. (1991). Hydrate of Carbon-Dioxide and Methane Mixtures. J. Chem. Eng. Data, 36, 68-71.
- [2] Behar, E., Delion, A.S., Herri, J.M., Sugier, A., Thomas, M. Plugging control of production facilities by hydrates. Annuals of the New York Academy of Sciences, 715, 94–105. ,(1994).
- [3] Chongwei Xiao, Hertanto Adidharma.: *Dual function inhibitors for methane hydrate*, Journal of University of Wyoming, Laramie, USA (2008).
- [4] Chongwei Xiao, Nico Wibisono, Hertanto Adidharma.: *Dialkylimidazolium halide ionic liquids as dual function inhibitors for methane hydrate* , Journal of University of Wyoming, Laramie, USA (2010).
- [5] Clark, L.W.; Frostman, L.M.; and Anderson. J., 2005. Low Dosage Hydrate Inhibitors (LDHI): Advances in Flow Assurance Technology for Offshore Gas Production Systems in the International Petroleum Technology Conference, Doha, Qatar, 21-23 November (2005).
- [6] Don. W. G. and Robert H. P., 2008. *Perry's Chemical Engineers' Handbook*. 8th Edition.
- [7] Jamaluddin, A., K., M., Kalogerakis, N., and Bishnoi, P., R., Hydrate Plugging Problems in Undersea Natural Gas Pipelines under Shutdown Conditions. Journal of Petroleum Science and Engineering, 5, 4, 323–335. (1991).
- [8] Khalik M. Sabil,. *Phase Behaviour, Thermodynamics and Kinetics of Clathrate Hydrate Systems of Carbon Dioxide in Presence of Tetrahydrofuran and Electrolytes*. PhD Thesis, Delft University of Technology, Netherland (2009).
- [9] Ki-Sub Kim, Jeong Wong Kang and Seong-Pil Kang, Chem. Commun., 47, 6341-6343 (2011).
- [10] Lee J.D. and Englezos P. 2005, *Enhancement of The Performance of Gas Hydrate Kinetic Inhibitor With Polyethylene Oxide*, British Columbia, Canada: Elsevier Ltd.
- [11] Sloan Jr., E.D. and Koh, C.A.. *Clathrate Hydrates of Natural Gas*, *third ed.*, CRC Press, Boca Raton , (2007).

- [12] Smith, J.M., Van Ness, H.C. & Abbott, M.M. Introduction to Chemical Engineering Thermodynamics. McGraw-Hill, 6. (2001).
- [13] Thi Phuong Thuy Pham , Chul-Woong Cho , Yeoung-Sang Yun. *Environmental fate and toxicity of ionic liquids : A review*, (2009).
- [14] Villano, L.D., Kelland, M.A.. Chem. Eng. Sci., 65, 5366–5372, (2010)
- [15] Wu D J, Hu Y F, Yang J T. *Natural Gas Industry*, 2000, 20(6): 95
- [16] Xiao-Sen Li, Yi-Jun Liu, Zhi-Yong Zeng, Zhao-Yang Chen, Gang Li, and Hui-Jie Wu.: Equilibrium Hydrate Formation Conditions for the Mixtures of Methane + Ionic Liquids + Water, A journal of Graduate University of Chinese Academy of Science, Beijing, P. R. China (2011).
- [17] Xiao, C., Wibisono, N., & Adidharma. H.. Dialkylimidazolium Halide Ionic Liquids as Dual Function Inhibitor for Methane Hydrate. Chemical Engineering Science, 65, 3080-3085. (2010)
- [18] Zhao Y, Ding J. *Natural Gas Industry*, 24(12):132, (2004).
- [19] Zhong. Y., Rogers. R.E. Surfactant Effects on Gas Hydrate Formation, Chem. Eng. Sci., 55, 4175–4187. (2000).

APPENDICES

- Appendix 1** Comparison of Properties of Ice, sI and sII Hydrates
- Appendix 2** Volume calculation for 1-Ethyl-3-methylimidazolium tetrafluoroborate, EMIM BF₄ at 0.1wt%, 0.5wt% and 1.0wt% concentration.
- Appendix 3** Illustration of hydrate formation and disassociation process
- Appendix 4** Material Safety Data Sheet (MSDS) from MERCK for EMIM BF₄

Comparison of Properties of Ice, sI, and sII Hydrates*

Property	Ice	Structure I	Structure II
Structure and dynamics			
Crystallographic unit cell space group	Positively	Pm3n	Fd3m
No. of H ₂ O molecules	4	46	136
Lattice parameters at 273 K (Å)	$a = 4.52, c = 7.56$	12.0	17.3
Dielectric constant at 273 K	92	~58	~58
Infrared spectrum	Peak at 220.5 cm ⁻¹	Peak at 229.3 cm ⁻¹	^b with others
H ₂ O concentration (wt% at 273 K (1) sI)	21	~10	~10
H ₂ O diffusion jump time (ps)	2.7	~2000	~2000
Mechanical properties			
Isothermal Young's modulus (at 268 K (10 ⁹ Pa)	9.5	8.4 ^{2d}	8.2 ^{2e}
Poisson's ratio	0.35(0) ^c	0.34(0) ^c	0.31(19) ^c
Bulk modulus (GPa)	8.8 (0.007) ^c	5.5 (0.762) ^c	6.482 ^c
Shear modulus (GPa)	3.9 (3.488) ^c	2.4 (2.574) ^c	3.6683 ^c
Compressional velocity, V_p (m/s)	3870 (1) ^d	3778 (1) ^b	3821.8 ^a
Shear velocity, V_s (m/s)	1929 ^c	1963.6	2001.14 ^b
Velocity ratio (compressant)	1.99	1.92	1.91
Thermal properties			
Linear thermal expansion (at 200 K (K ⁻¹))	56×10^{-6}	77×10^{-6}	52×10^{-6}
Thermal conductivity (Wm ⁻¹ K ⁻¹) (at 263 K)	2.23	0.49 ± 0.02	0.51 ± 0.02
	2.18 ± 0.04 ^c	0.51 ± 0.03 ^c	0.50 ± 0.03 ^c
Adiabatic bulk compression (at 273 K (GPa)	12	14 ^{2d}	14 ^{2e}
Heat capacity (Jkg ⁻¹ K ⁻¹)	1700 ± 200	2080	2130 ± 40 ^c
Refractive index (632.8 nm, +3 °C)	1.3082 ^c	1.346 ^c	1.350 ^c
Density (g/cm ³)	0.91 ^c	0.94 (also see Example 5.2)	1.291 ^c

* Note: Unless indicated, values are from Davidson (1983), Davidson et al. (1986) and Rippeester et al. (1994).

^a Helys and et al. (2002) at 253–268 K, 22.4–32.8 MPa (ice, Ih); 258–288 K, 27.6–62.1 MPa (CH₄, sI); 258–288 K, 50.5–91.6 MPa (CH₄–C₂H₆, sII).

^b Helys and et al. (2003) at 258–288 K, 26.6–62.1 MPa.

^c Wang et al. (2005) at 248–268 K (ice Ih); 253–288 K (CH₄, sI); 248–265.5 K (THF, sII).

^d Huang and Fan (2004) for CH₄, sI.

^e Bykov and Rasmussen (1997).

^f Fractional occupancy (calculated from a theoretical model) in small (S) and large (L) cavities. sI = CH₄: 0.87 (S) and CH₄: 0.973 (L); sII = CH₄: 0.672 (S), 0.057 (L), C₂H₆: 0.096 (L) only C₂H₆: 0.84 (L) only.

Volume calculation for different concentrations (0.1wt%, 0.5wt% & 1.0wt%) of
1-Ethyl-3-methylimidazolium tetrafluoroborate, EMIM BF₄

Basis of 100kg solution :	Mass of EMIM BF ₄ = 0.1 kg	Mass of H ₂ O kg	= 99.9
---------------------------	--	--------------------------------	--------

$$\begin{aligned} \text{Moles Fraction, } x &= \frac{n \text{ EMIM BF}_4}{n \text{ EMIM BF}_4 + n \text{ H}_2\text{O}} \\ \text{EMIM BF}_4 &= \frac{0.505127039 \text{ mol}}{0.505127039 \text{ mol} + 5550 \text{ mol}} \\ &= 0.000091005 \end{aligned}$$

$$\begin{aligned} \text{Volume Fraction, } x &= \frac{\text{Volume of EMIM BF}_4}{\text{Volume of H}_2\text{O}} \\ \text{Volume of EMIM BF}_4 &= \text{Volume of H}_2\text{O} \times x \text{ value of EMIM BF}_4 \\ &= 130 \text{ ml} \times 0.000091005 \\ &= 0.01183065 \text{ ml} \\ &= 11.83 \mu\text{l} \end{aligned}$$

Basis of 100kg solution :	Mass of EMIM BF ₄ = 0.5 kg	Mass of H ₂ O kg	= 99.5
---------------------------	--	--------------------------------	--------

$$\begin{aligned} \text{Moles Fraction, } x &= \frac{n \text{ EMIM BF}_4}{n \text{ EMIM BF}_4 + n \text{ H}_2\text{O}} \\ \text{EMIM BF}_4 &= \frac{2.525635197 \text{ mol}}{2.525635197 \text{ mol} + 5527.7778 \text{ mol}} \\ &= 0.00045669 \end{aligned}$$

$$\begin{aligned} \text{Volume Fraction, } x &= \frac{\text{Volume of EMIM BF}_4}{\text{Volume of H}_2\text{O}} \\ \text{Volume of EMIM BF}_4 &= \text{Volume of H}_2\text{O} \times x \text{ value of EMIM BF}_4 \\ &= 130 \text{ ml} \times 0.00045669 \\ &= 0.05936972187 \text{ ml} \\ &= 59.37 \mu\text{l} \end{aligned}$$

iii. At 1.0 wt% of EMIM BF₄

Basis of 100kg solution : Mass of EMIM BF₄ = 1.0 kg Mass of H₂O = 99.0 kg

$$\begin{array}{llll} \text{Number of moles, } n, & = \frac{1.0 \text{ kg EMIM BF}_4}{197.97 \frac{\text{kg}}{\text{mol}}} & \text{Number of moles, } n, & = \frac{99.0 \text{ kg H}_2\text{O}}{18 \frac{\text{kg}}{\text{mol}}} \\ \text{for EMIM BF}_4 & = 5.051270395 \times 10^{-3} \text{ k mol} & \text{for H}_2\text{O} & = 5.5 \text{ k mol} \\ & = 5.051270395 \text{ mol} & & = 5500 \text{ mol} \end{array}$$

$$\text{Moles Fraction, } x = \frac{n \text{ EMIM BF}_4}{n \text{ EMIM BF}_4 + n \text{ H}_2\text{O}}$$

$$\begin{aligned} \text{EMIM BF}_4 &= \frac{5.051270395 \text{ mol}}{5.051270395 \text{ mol} + 5500 \text{ mol}} \\ &= 0.00091757 \end{aligned}$$

Moles Fraction = Volume Fraction

$$\text{Volume Fraction, } x = \frac{\text{Volume of EMIM BF}_4}{\text{Volume of H}_2\text{O}}$$

$$\text{Volume of EMIM BF}_4 = \text{Volume of H}_2\text{O} \times x \text{ value of EMIM BF}_4$$

$$= 130 \text{ ml} \times 0.00091757$$

$$= 0.1192841118 \text{ ml}$$

$$= 119.28 \mu\text{l}$$

	0.1 wt % EMIM BF ₄	0.5 wt % EMIM BF ₄	1.0 wt % EMIM BF ₄
Volume of Ionic Liquid, EMIM BF ₄ (130 ml H ₂ O)	11.83 μl	59.37 μl	119.28 μl

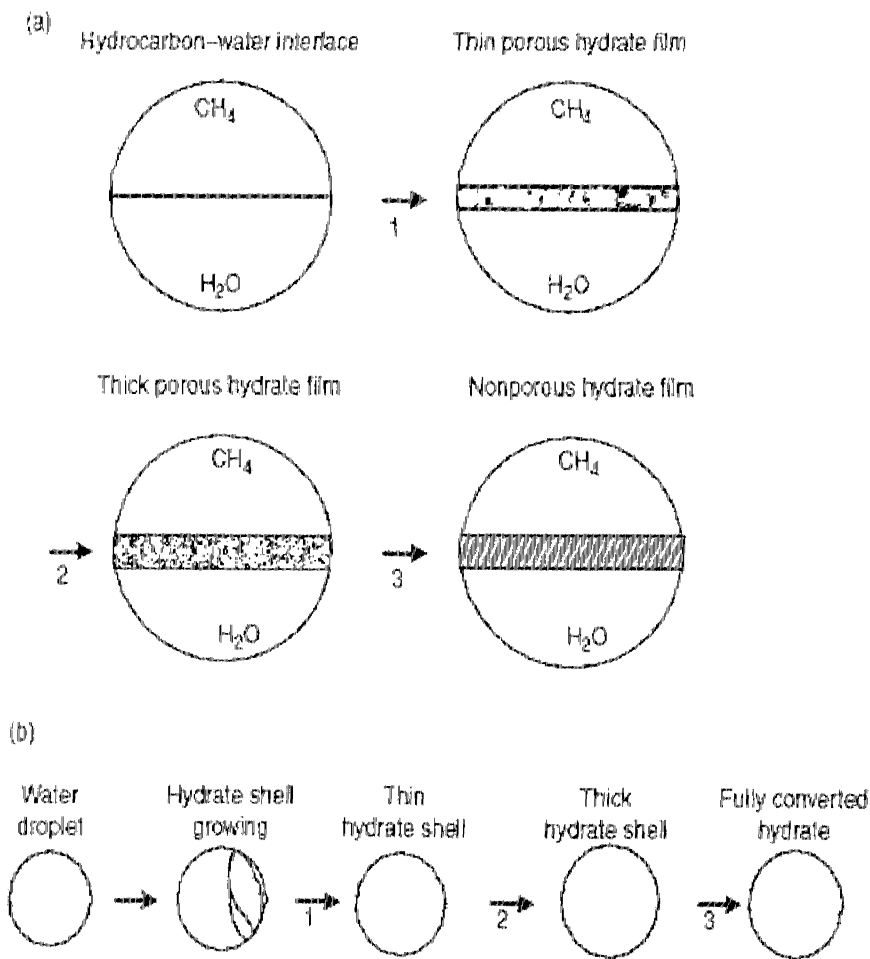


FIGURE 3.28 (a) Schematic of the proposed mechanism for hydrate film formation at a hydrocarbon–water interface. Step 1: Propagation of a thin porous hydrate film across the hydrocarbon–water interface. Step 2: Film development. Step 3: Hydrate film solidification (Taylor, 2006; Subramanian, 2000) and (b) Schematic of the proposed mechanism for hydrate formation from a water droplet. Step 1: Propagation of a thin porous hydrate shell (film) around the water droplet. Step 2: Shell development. Step 3: Bulk conversion of the droplet interior to hydrate (Taylor, 2006).

Source: Sloan Jr., E.D. and Koh, C.A., 2007. Clathrate Hydrates of Natural Gas, third ed., CRC Press, Boca Raton

Appendix 4

Material Safety Data Sheet (MSDS) from MERCK for EMIM BF₄

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

Revision Date 05.11.2010

Version 3.8

1. Identification of the substance/mixture and of the company/undertaking

1.1 Product identifier

Catalogue No. 490037

Product name 1-Ethyl-3-methylimidazolium tetrafluoroborate for synthesis

REACH Registration Number A registration number is not available for this substance as the substance or its use are exempted from registration according to Article 2 REACH Regulation (EC) No 1907/2006, the annual tonnage does not require a registration or the registration is envisaged for a later registration deadline.

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses Reagent for development and research
For additional information on uses please refer to the Merck Chemicals portal (www.merck-chemicals.com).

1.3 Details of the supplier of the safety data sheet

Company Merck KGaA * 64271 Darmstadt * Germany * Phone: +49 6151 72-0

Responsible Department EQ-EPS * e-mail: prodsafe@merck.de

1.4 Emergency telephone number Please contact the regional Merck representation in your country.

2. Hazards identification

2.1 Classification of the substance or mixture

Classification (REGULATION (EC) No 1272/2008)

Skin irritation, Category 2, H315

Eye irritation, Category 2, H319

For the full text of the H-Statements mentioned in this Section, see Section 16.

Classification (67/548/EEC or 1999/45/EC)

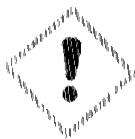
Xi; R36/38

For the full text of the R-phrases mentioned in this Section, see Section 16.

2.2 Label elements

Labelling (REGULATION (EC) No 1272/2008)

Hazard pictograms



Signal word
Warning

Catalogue No.	490037
Product name	1-Ethyl-3-methylimidazolium tetrafluoroborate for synthesis

Hazard statements

H315 Causes skin irritation.
H319 Causes serious eye irritation.

Precautionary statements

P302 + P352 IF ON SKIN: Wash with plenty of soap and water.
P305 + P351 + P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

Reduced labelling (≤125 ml)

Hazard pictograms



Signal word
Warning

CAS-No. 143314-16-3

Labelling (67/548/EEC or 1999/45/EC)

Symbol(s) Xi Irritant

R-phrases(s) 36/38 Irritating to eyes and skin.

Further information

Caution - substance not yet fully tested.

Reduced labelling (≤125 ml)

Symbol(s) Xi Irritant

2.3 Other hazards

None known.

3. Composition/information on ingredients

Formula	$C_6H_{11}N_2 \cdot BF_4$	$C_6H_{11}BF_4N_2$ (Hill)
CAS-No.	143314-16-3	
Molar mass	197,97 g/mol	

4. First aid measures

4.1 Description of first aid measures

After inhalation: fresh air. Consult doctor if feeling unwell.

After skin contact: wash off with plenty of water. Remove contaminated clothing.

After eye contact: rinse out with plenty of water. Call in ophthalmologist.

After swallowing: immediately make victim drink water (two glasses at most). Consult a physician.

4.2 Most important symptoms and effects, both acute and delayed irritant effects

Catalogue No. 490037
Product name 1-Ethyl-3-methylimidazolium tetrafluoroborate for synthesis

The following applies to boron compounds in general: resorption is followed by nausea and vomiting, agitation (>, <) spasms, CNS disorders, cardiovascular disorders.

4.3 Indication of immediate medical attention and special treatment needed
No information available.

5. Fire-fighting measures

5.1 Extinguishing media

Suitable extinguishing media

Water, Carbon dioxide (CO₂), Foam, Dry powder

Unsuitable extinguishing media

For this substance/mixture no limitations of extinguishing agents are given.

5.2 Special hazards arising from the substance or mixture

Combustible material

Vapours are heavier than air and may spread along floors.

Forms explosive mixtures with air on intense heating.

Development of hazardous combustion gases or vapours possible in the event of fire.

Fire may cause evolution of:

Hydrogen fluoride, nitrogen oxides

5.3 Advice for firefighters

Special protective equipment for fire-fighters

Stay in danger area only with self-contained breathing apparatus. Prevent skin contact by keeping a safe distance or by wearing suitable protective clothing.

Further information

Suppress (knock down) gases/vapours/mists with a water spray jet. Prevent fire extinguishing water from contaminating surface water or the ground water system.

6. Accidental release measures

6.1 Personal precautions, protective equipment and emergency procedures

Advice for non-emergency personnel: Avoid substance contact. Do not breathe vapours, aerosols. Ensure adequate ventilation. Evacuate the danger area, observe emergency procedures, consult an expert.

Advice for emergency responders: Protective equipment see section 8.

6.2 Environmental precautions

Do not empty into drains.

6.3 Methods and materials for containment and cleaning up

Cover drains. Collect, bind, and pump off spills.

Observe possible material restrictions (see sections 7.2 and 10.5).

Take up with liquid-absorbent material (e.g. Chemizorb®). Dispose of properly. Clean up affected area.

6.4 Reference to other sections

Indications about waste treatment see section 13.

7. Handling and storage

7.1 Precautions for safe handling

Observe label precautions.

Catalogue No.	490037
Product name	1-Ethyl-3-methylimidazolium tetrafluoroborate for synthesis

7.2 Conditions for safe storage, including any incompatibilities

Tightly closed.

Store at +15°C to +25°C.

7.3 Specific end uses

Apart from the uses mentioned in section 1.2 no other specific uses are stipulated.

8. Exposure controls/personal protection

8.1 Control parameters

8.2 Exposure controls

Engineering measures

Technical measures and appropriate working operations should be given priority over the use of personal protective equipment.

See section 7.1.

Individual protection measures

Protective clothing needs to be selected specifically for the workplace, depending on concentrations and quantities of the hazardous substances handled. The chemical resistance of the protective equipment should be enquired at the respective supplier.

Hygiene measures

Immediately change contaminated clothing. Apply preventive skin protection. Wash hands and face after working with substance.

Eye/face protection

Safety glasses

Hand protection

full contact:

Glove material:	Nitrile rubber
Glove thickness:	0,11 mm
Break through time:	> 480 min

splash contact:

Glove material:	Nitrile rubber
Glove thickness:	0,11 mm
Break through time:	> 480 min

The protective gloves to be used must comply with the specifications of EC Directive 89/686/EEC and the related standard EN374, for example KCL 741 Dermatril® L (full contact), KCL 741 Dermatril® L (splash contact).

This recommendation applies only to the product stated in the safety data sheet<(>,<)> supplied by us and for the designated use. When dissolving in or mixing with other substances and under conditions deviating from those stated in EN374 please contact the supplier of CE-approved gloves (e.g. KCL GmbH, D-36124 Eichenzell, Internet: www.kcl.de).

Other protective equipment:

protective clothing

Respiratory protection

required when vapours/aerosols are generated.

Catalogue No.	490037
Product name	1-Ethyl-3-methylimidazolium tetrafluoroborate for synthesis

Environmental exposure controls
Do not empty into drains.

1. Physical and chemical properties

9.1 Information on basic physical and chemical properties

Form	liquid
Colour	tan
Odour	weak
Odour Threshold	No information available.
pH	5 at 20 °C
Melting point	15 °C
Boiling point/boiling range	> 350 °C at 1.013 hPa
Flash point	> 110 °C
Evaporation rate	No information available.
Flammability (solid, gas)	No information available.
Lower explosion limit	No information available.
Upper explosion limit	No information available.
Vapour pressure	No information available.
Relative vapour density	No information available.
Relative density	1,34 g/cm ³ at 20 °C
Water solubility	No information available.
Partition coefficient: n-octanol/water	No information available.
Autoignition temperature	No information available.
Decomposition temperature	No information available.
Viscosity, dynamic	No information available.
Explosive properties	No information available.
Oxidizing properties	No information available.

9.2 Other data

none

Catalogue No.	490037
Product name	1-Ethyl-3-methylimidazolium tetrafluoroborate for synthesis

10. Stability and reactivity

10.1 Reactivity

Forms explosive mixtures with air on intense heating.

10.2 Chemical stability

The product is chemically stable under standard ambient conditions (room temperature) .

10.3 Possibility of hazardous reactions

Violent reactions possible with:

Strong oxidizing agents

10.4 Conditions to avoid

Strong heating.

A range from approx. 15 Kelvin below the flash point is to be rated as critical.

10.5 Incompatible materials

no information available

10.6 Hazardous decomposition products

in the event of fire: See chapter 5.

11. Toxicological information

11.1 Information on toxicological effects

Acute oral toxicity

Symptoms: Irritations of mucous membranes in the mouth, pharynx, oesophagus and gastrointestinal tract.

Acute inhalation toxicity

Symptoms: Possible damages:, mucosal irritations

Skin irritation

Causes skin irritation.

Eye irritation

Causes serious eye irritation.

Specific target organ toxicity - single exposure

The substance or mixture is not classified as specific target organ toxicant, single exposure.

Specific target organ toxicity - repeated exposure

The substance or mixture is not classified as specific target organ toxicant, repeated exposure.

Aspiration hazard

No aspiration toxicity classification

11.2 Further information

Further information

Quantitative data on the toxicity of this product are not available.

Other information

The following applies to boron compounds in general: resorption is followed by nausea and vomiting, agitation(>, <)> spasms, CNS disorders, cardiovascular disorders.

Further data:

Other dangerous properties can not be excluded.

Handle in accordance with good industrial hygiene and safety practice.

Catalogue No. 490037
Product name 1-Ethyl-3-methylimidazolium tetrafluoroborate for synthesis

12. Ecological information

12.1 Toxicity

No information available.

12.2 Persistence and degradability

No information available.

12.3 Bioaccumulative potential

No information available.

12.4 Mobility in soil

No information available.

12.5 Results of PBT and vPvB assessment

PBT/vPvB assessment not available as chemical safety assessment not required/not conducted.

12.6 Other adverse effects

Additional ecological information

We have no quantitative data concerning the ecological effects of this product.

Further information on ecology

Do not allow to run into surface waters, wastewater, or soil.

13. Disposal considerations

Waste treatment methods

See www.retrologistik.com for processes regarding the return of chemicals and containers, or contact us there if you have further questions.

14. Transport information

Not classified as dangerous in the meaning of transport regulations.

15. Regulatory information

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

EU regulations

Major Accident Hazard
Legislation

96/82/EC

Directive 96/82/EC does not apply

Occupational restrictions

Take note of Dir 94/33/EC on the protection of young people at work.

National legislation

Storage class VCI

10 Combustible liquids not in Storage Class 3

15.2 Chemical Safety Assessment

For this product a chemical safety assessment was not carried out.

16. Other information

Full text of H-Statements referred to under sections 2 and 3.

H315

Causes skin irritation.

H319

Causes serious eye irritation.

according to Regulation (EC) No. 1907/2006

Catalogue No.	490037
Product name	1-Ethyl-3-methylimidazolium tetrafluoroborate for synthesis

Full text of R-phrases referred to under sections 2 and 3

R36/38 Irritating to eyes and skin.

Training advice

Provide adequate information, instruction and training for operators.

Regional representation: This information is given on the authorised Safety Data Sheet for your country.

Key or legend to abbreviations and acronyms used in the safety data sheet

Used abbreviations and acronyms can be looked up at www.wikipedia.org.

The information contained herein is based on the present state of our knowledge. It characterises the product with regard to the appropriate safety precautions. It does not represent a guarantee of any properties of the product.